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L Number	Hits	Search Text	DB	Time stamp
1	103	(water adj chemistry) and reactor and crack	USPAT; US-PGPUB	2004/02/26 15:00
2	16	(water adj chemistry) and reactor and ((predict\$ or estimat\$) near5 crack)	USPAT; US-PGPUB	2004/02/26 15:01



US005817958A

United States Patent [19]

Uchida et al.

[11] **Patent Number:** 5,817,958[45] **Date of Patent:** Oct. 6, 1998

[54] **PLANT MONITORING AND DIAGNOSING METHOD AND SYSTEM, AS WELL AS PLANT EQUIPPED WITH THE SYSTEM**

5,311,562 5/1994 Palusamy et al. .

[75] **Inventors:** Shunsuke Uchida; Haruo Fujimori, both of Hitachi; Fumlnobu Takahashi, Katsuta; Takaharu Fukuzaki, Hitachi; Izumi Yamada, Ibaraki-ken, all of Japan

Primary Examiner—Robert Raevis
Attorney, Agent, or Firm—Bardehle, Pagenberg, Dost, Altenburg, Frohwitter, Geissler

[57] **ABSTRACT**

Plant operating conditions 1, apparatus operating conditions 2 and environment conditions 3 are accumulated, combined and put together as a set of plant status variables 8 through a monitor 6, while water chemistry information 4 is accumulated as another set of plant status variables 9. The set of status variables 8 is updated and the past data are accumulated in the set of status variables 9. Periodical inspection data 5 are also accumulated in the set of status variables 9 along with the water chemistry information 4. The set 9 is compressed and stored as a plant chart 11 such as a personal clinical chart. A status variable prediction 12 is performed in consideration of the personality of a plant. Both data of the sets 8 and 10 are compared with each other by comparison means 13. If both the data nearly coincide with each other, the plant is diagnosed to the normal and, if not, it is diagnosed to be abnormal. When the plant is diagnosed to abnormal, an abnormal apparatus and an abnormal factor are identified.

[73] **Assignee:** Hitachi, Ltd., Tokyo, Japan

[21] **Appl. No.:** 691,007

[22] **Filed:** Aug. 5, 1996

Related U.S. Application Data

[63] Continuation of Ser. No. 247,039, May 20, 1994, Pat. No. 5,623,109.

[51] **Int. Cl.⁶** G21C 7/36

[52] **U.S. Cl.** 73/865.9

[58] **Field of Search** 73/799, 865.8, 73/866, 865.9; 376/215, 216, 245; 364/507

[56] **References Cited****U.S. PATENT DOCUMENTS**

5,159,563 10/1992 Miller et al. .

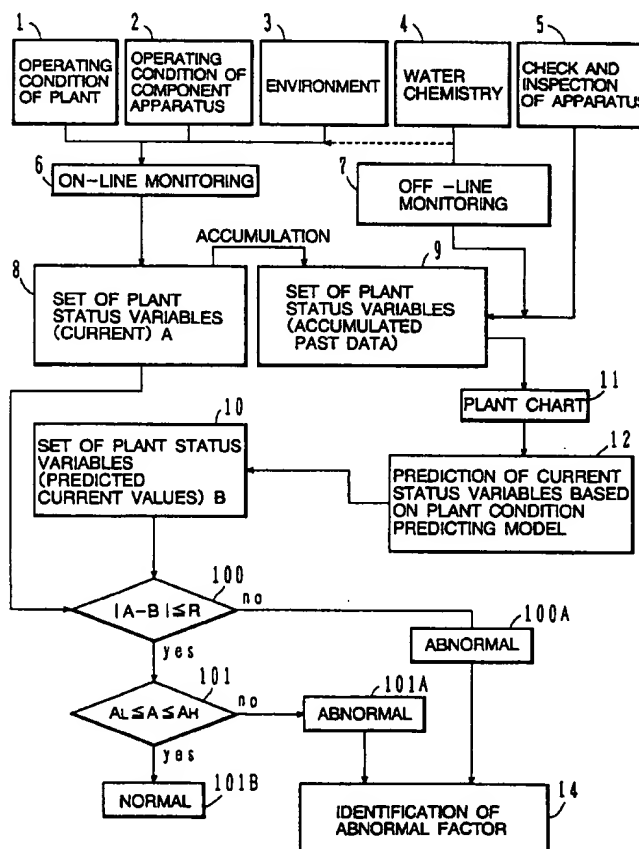
8 Claims, 20 Drawing Sheets

FIG. 1

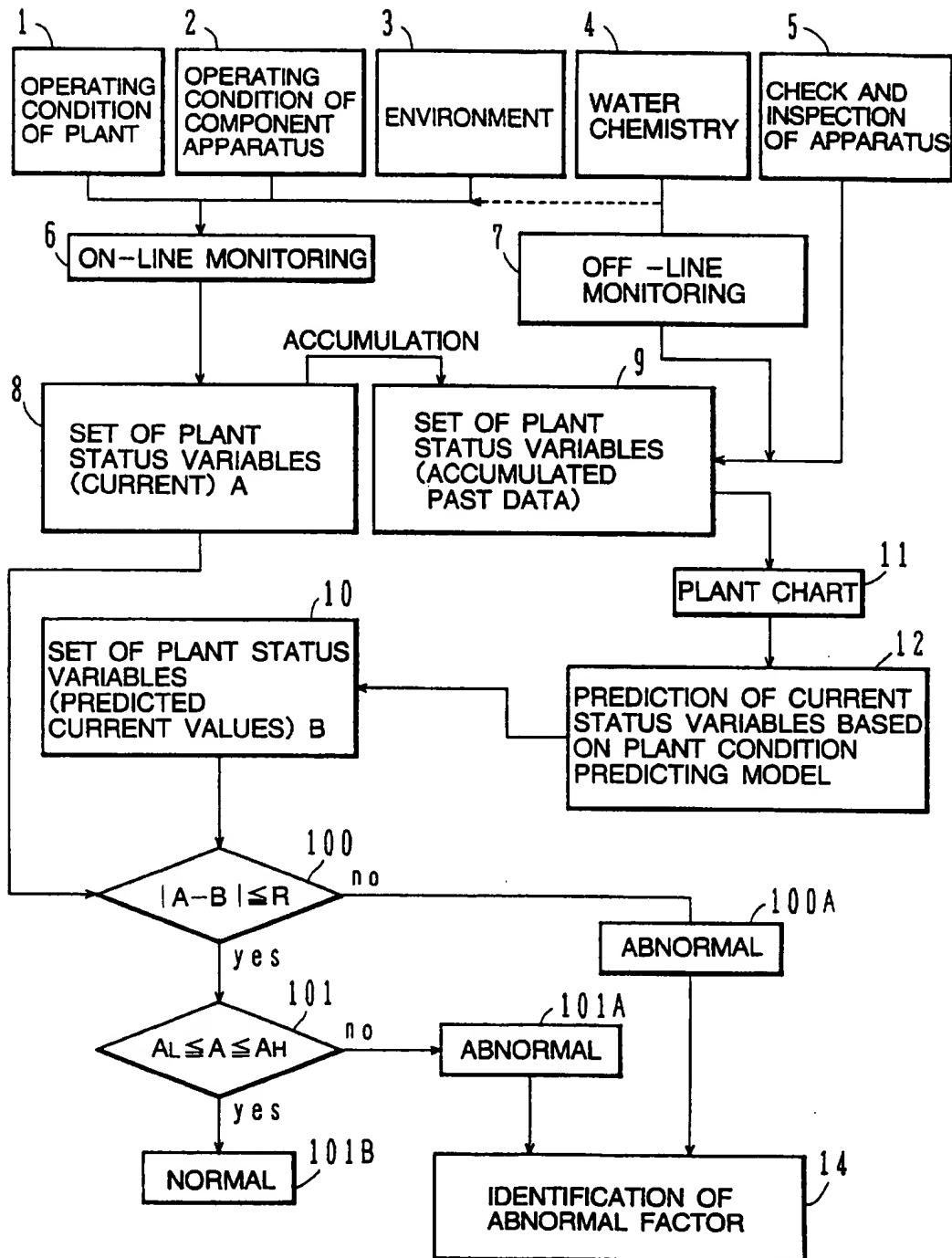


FIG. 2

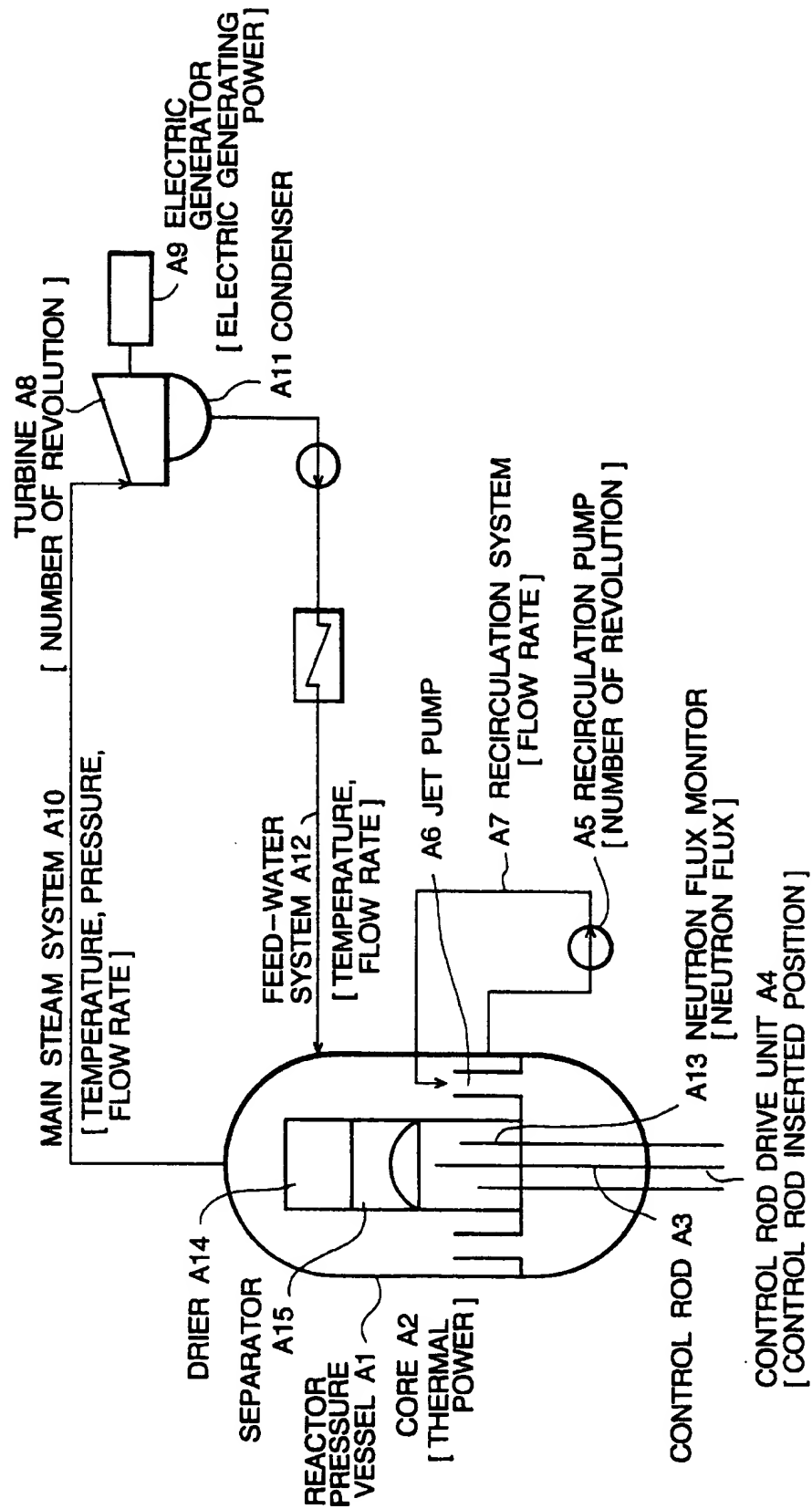


FIG.3
DIAGNOSIS FLOW FOR RECIRCULATION PUMP

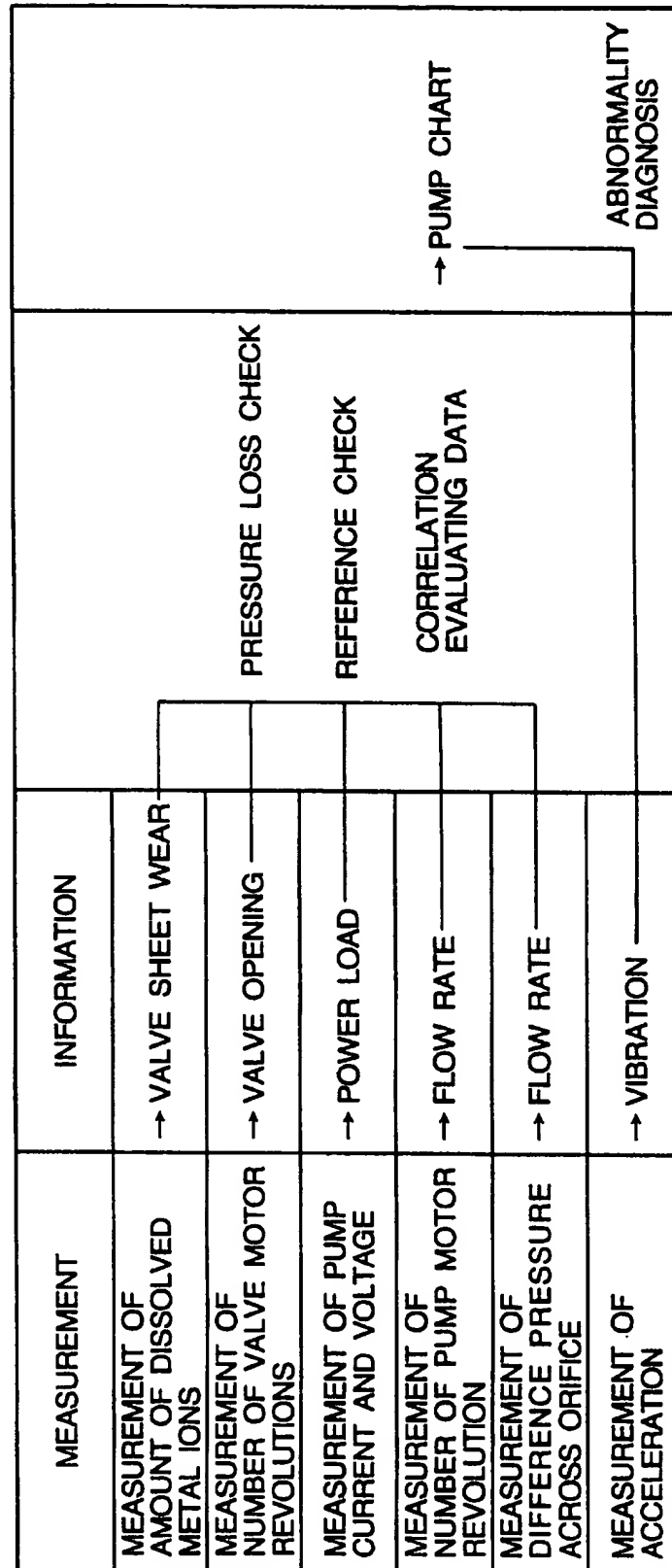


FIG. 4

EXAMPLE OF PLANT CHART
FOR RECIRCULATION PUMP DIAGNOSIS

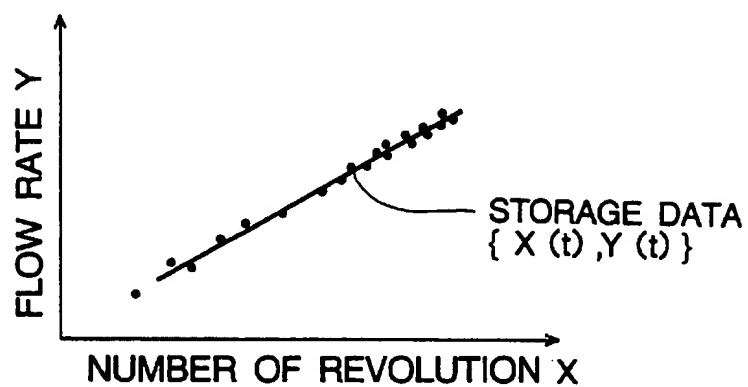


FIG.5
DIAGNOSIS FLOW OF PLANT THERMAL POWER

MEASUREMENT	INFORMATION	THERMAL POWER
VOLTAGE AND CURRENT ON GENERATOR	ELECTRIC GENERATING POWER	THERMAL POWER (1)
TEMPERATURE PRESSURE AND FLOW RATE OF MAIN STEAM		THERMAL POWER (2)
NEUTRON FLUX	NUCLEAR FISSION RATE	THERMAL POWER (3)
CONTROL ROD INSERTED POSITION		THERMAL POWER (4)
FLOW RATE RECIRCULATED		
TEMPERATURE AND FLOW RATE OF FEED-WATER		

FIG. 6A

EXAMPLE OF PLANT CHART
FOR THERMAL POWER DIAGNOSIS

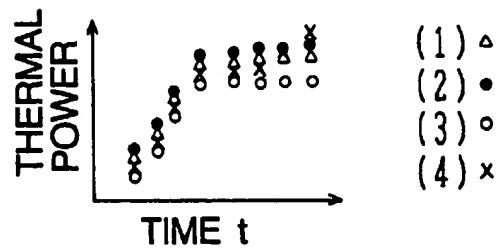


FIG. 6B

EXAMPLE OF PLANT CHART
FOR THERMAL POWER DIAGNOSIS

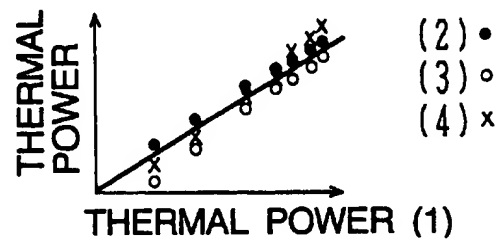


FIG. 7

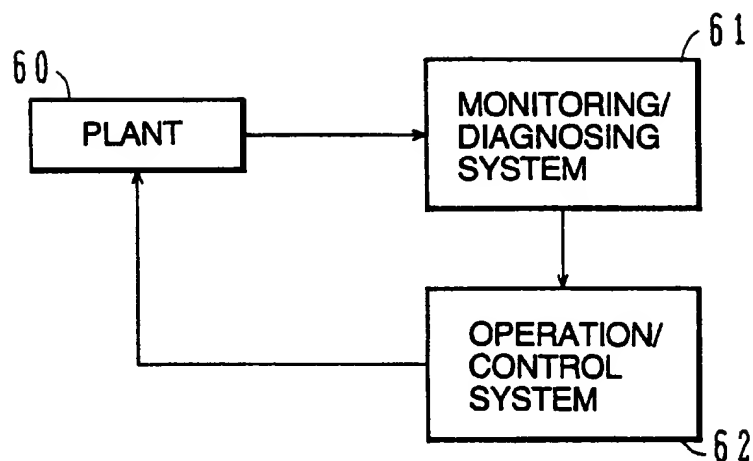


FIG. 8

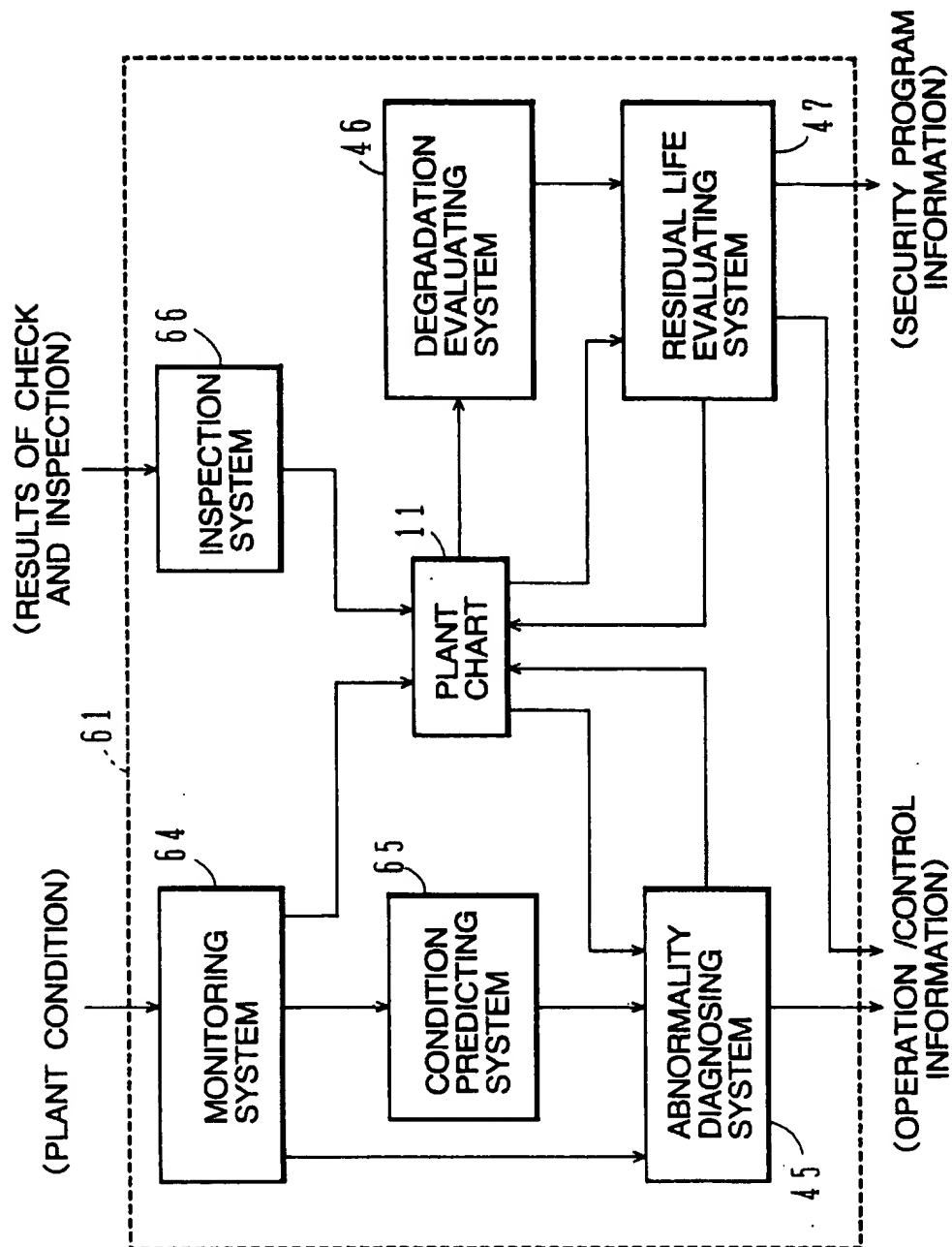


FIG. 9

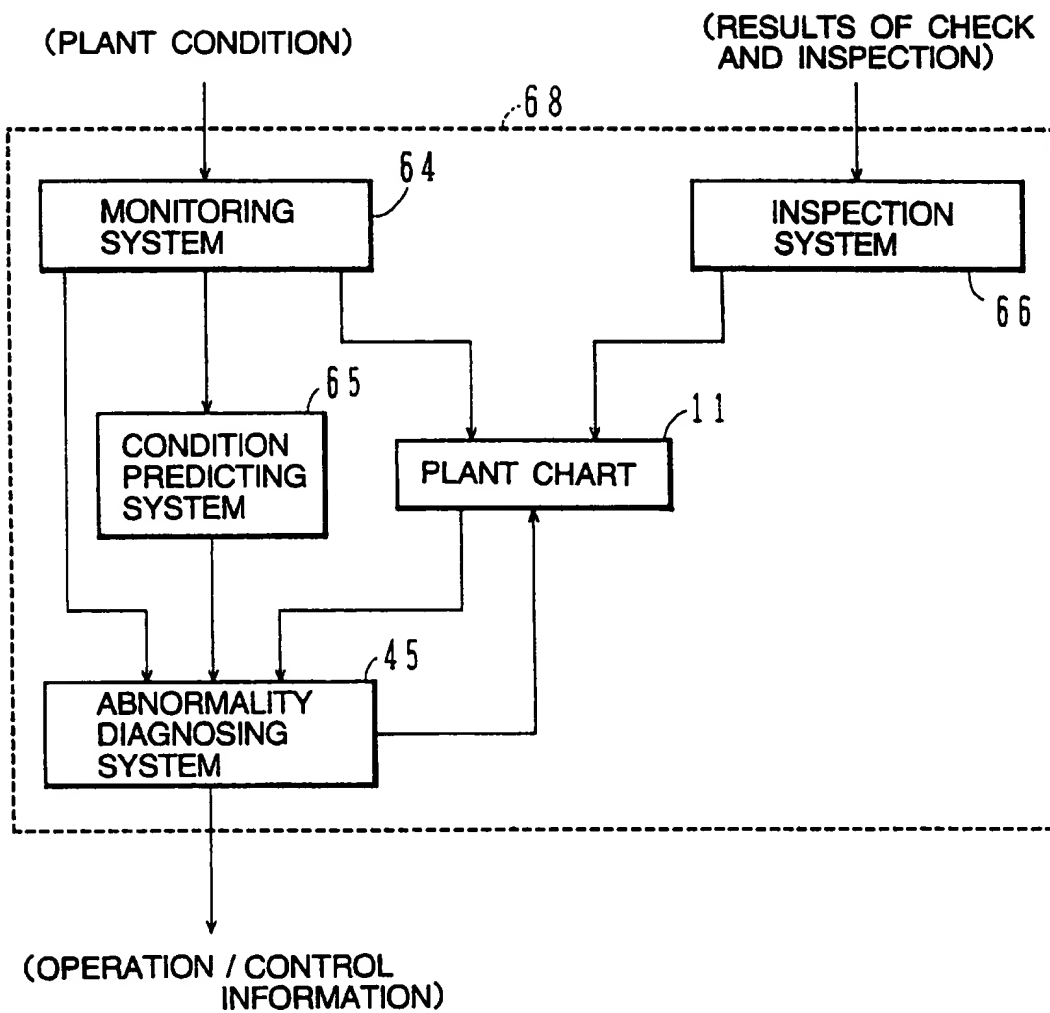


FIG.10

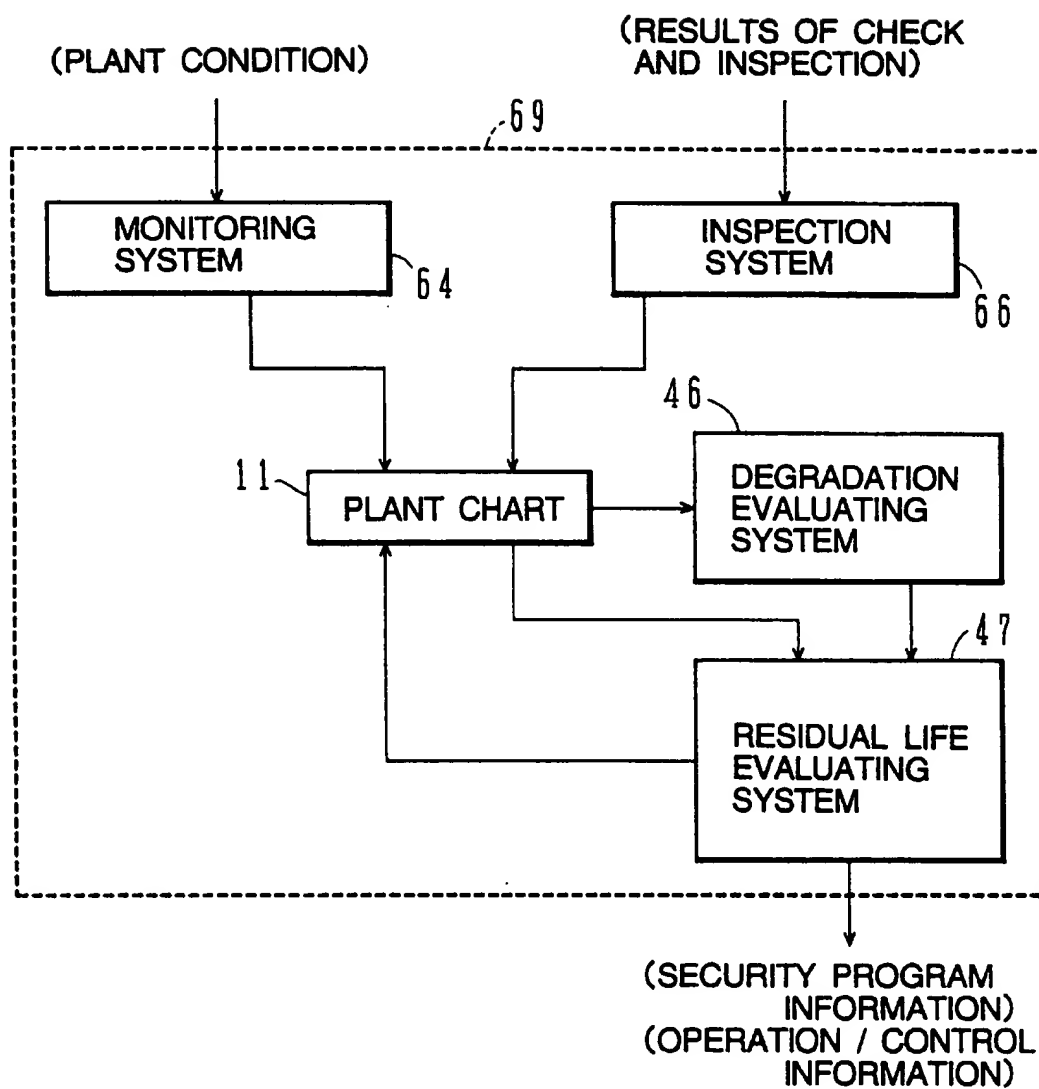


FIG. 11

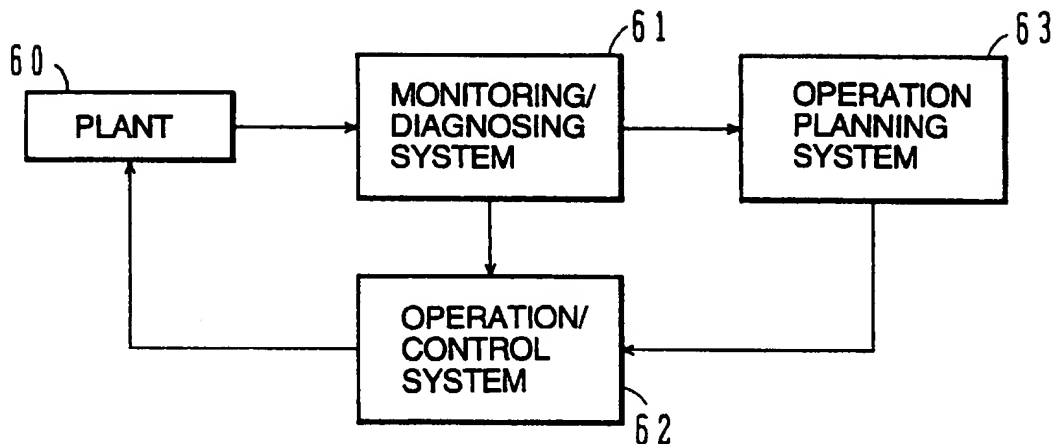


FIG. 12

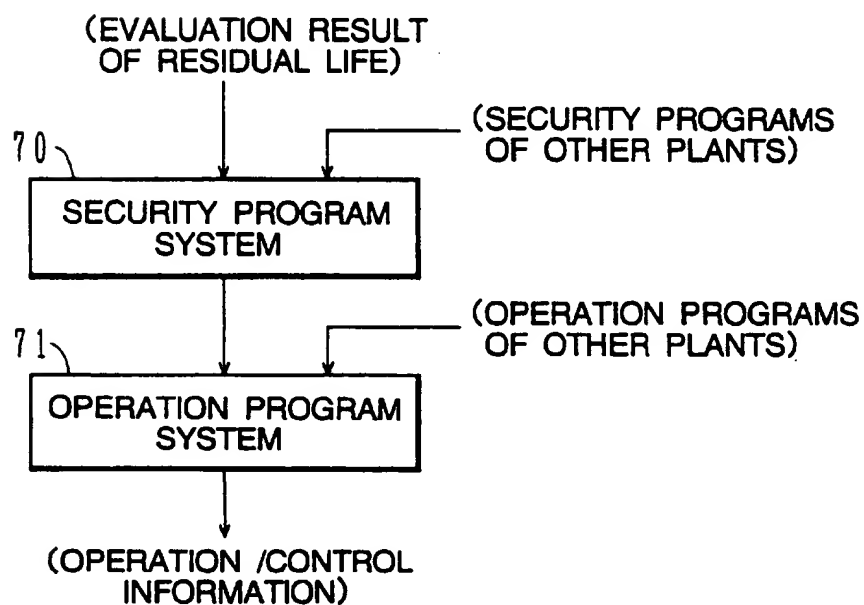
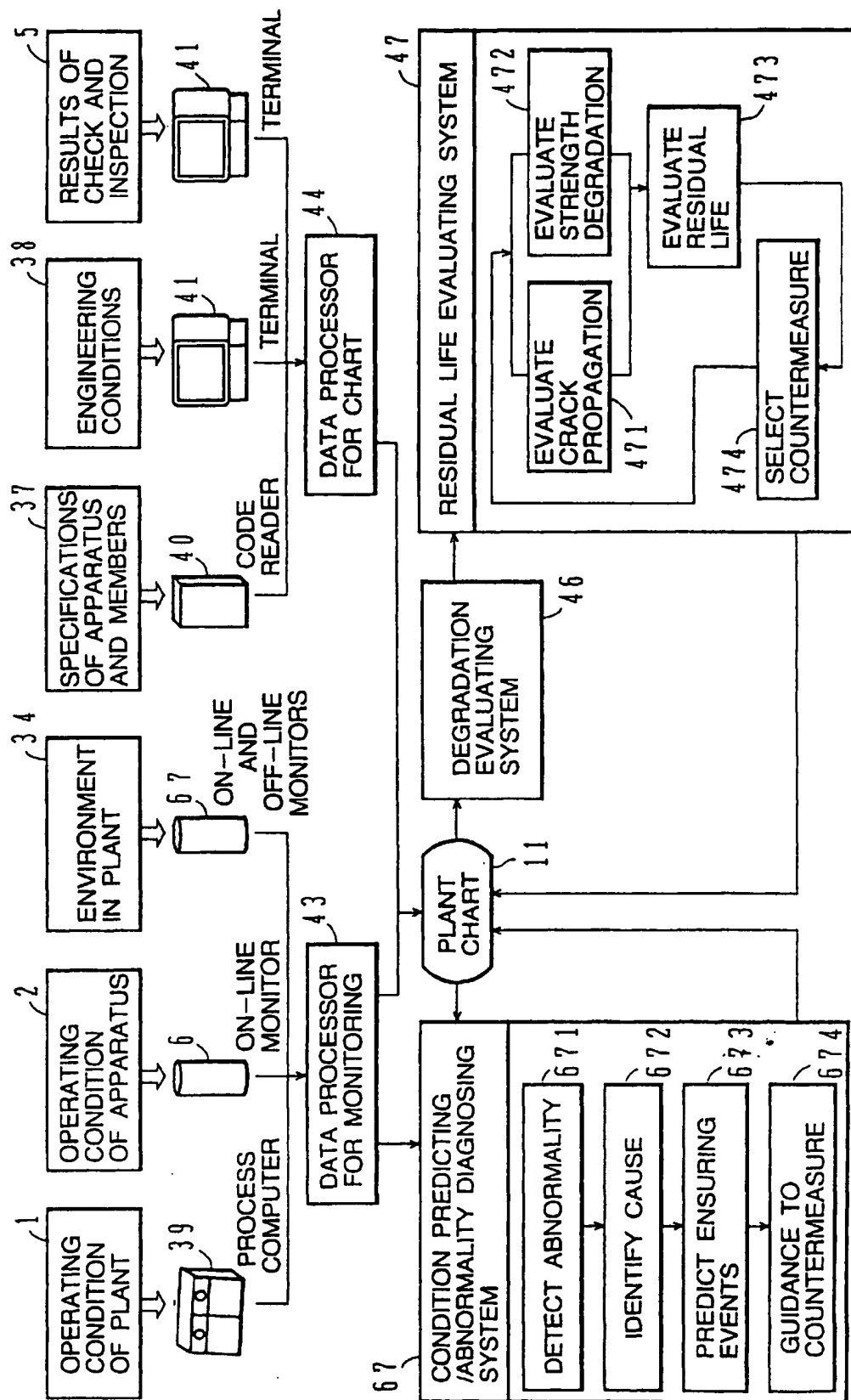


FIG. 13



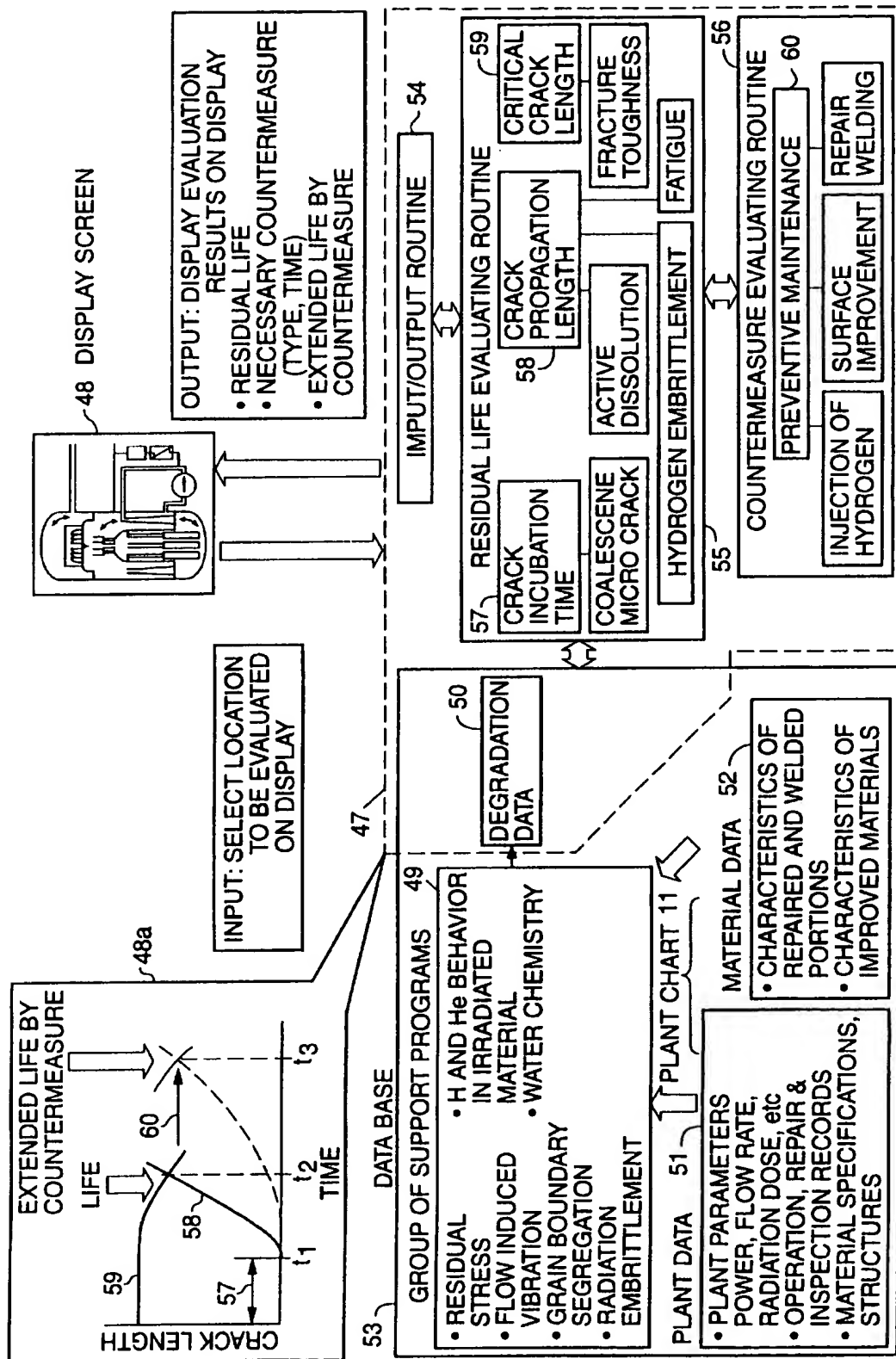
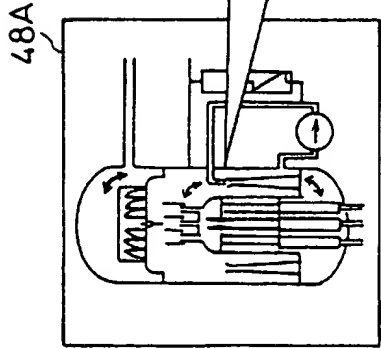
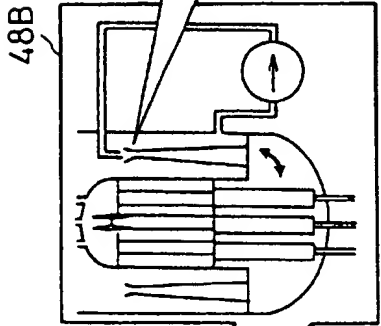


FIG. 15A



SELECTIVELY
ENLARGED

FIG. 15B



SELECTIVELY
ENLARGED

FIG. 15C

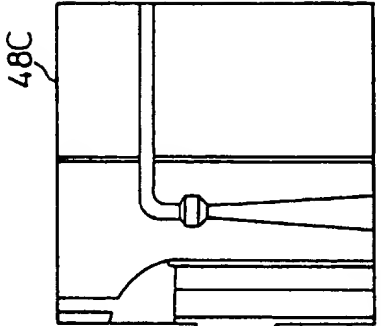


FIG. 16

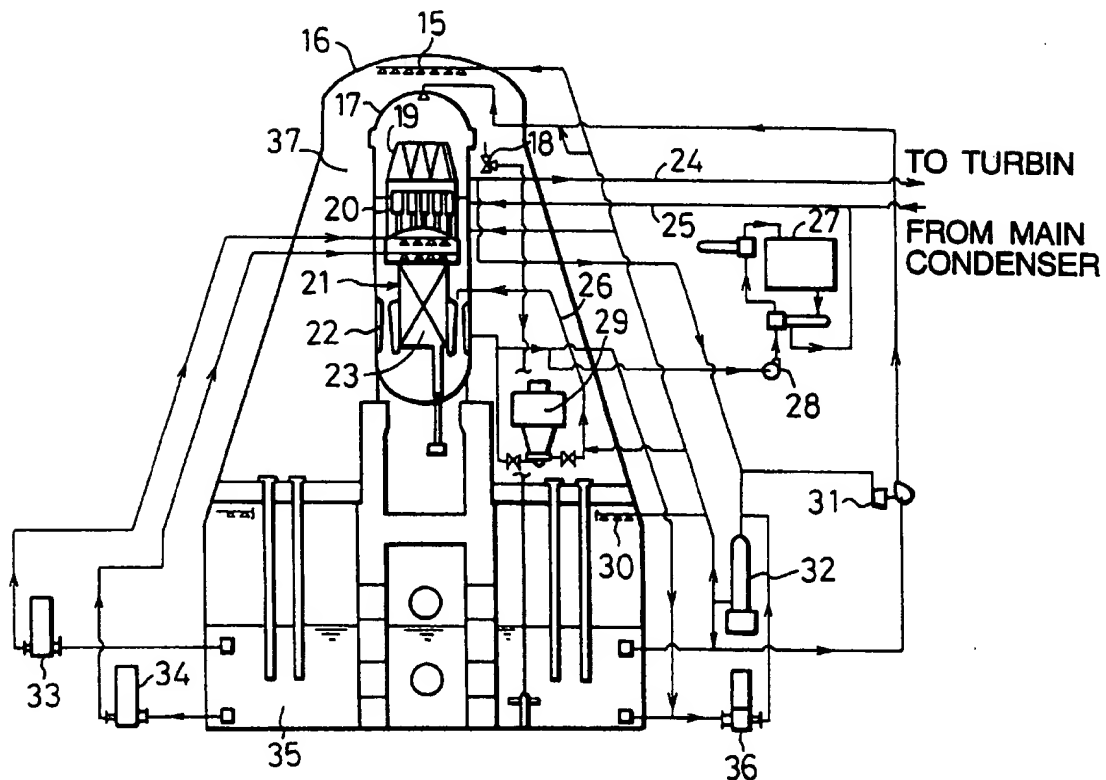
MAIN APPARATUS AND EQUIPMENT
IN BWR POWER PLANT

FIG.17A

TABLE OF MAIN APPARATUS AND EQUIPMENT OF REACTOR

APPARATUS AND EQUIPMENT TO BE DIAGNOSED		MAIN FUNCTION
APPARATUS / STATIC STRUCTURE	PRESSURE VESSEL	CONTAINMENT OF HIGH-TEMPERATURE , HIGH-PRESSURE COOLING WATER
	MAIN PIPES	CONTAINMENT OF HIGH-TEMPERATURE , HIGH-PRESSURE COOLING WATER
	CONTAINMENT VESSEL	AIR TIGHTNESS AND PRESSURE RESISTANCE
	REACTOR-INTERNALS	SUSTAINMENT OF RECIRCULATION FLOW RATE (JET PUMP)
	FUEL ASSEMBLY	CONTAINMENT OF RADIOACTIVE FISSION PRODUCTS
	COOLING WATER PURIFYING EQUIPMENT	REMOVAL OF IMPURITIES IN COOLING WATER

FIG. 17B

TABLE OF METHODS FOR DIAGNOSING MAIN APPARATUS AND EQUIPMENT OF REACTOR

APPARATUS AND EQUIPMENT TO BE DIAGNOSED	DIAGNOSING METHOD		
	OPERATING PERFORMANCE	ABNORMAL SIGNS	MATERIAL DETERIORATION
STATIC STRUCTURE / APPARATUS	■ PRESSURE RESISTANCE, LEAK TEST	■ NONDESTRUCTIVE INSPECTION	■ SURVEILLANCE WIRE
		■ NONDESTRUCTIVE INSPECTION ● STEAM LEAK DETECTION	□ SQUID □ ATOM PROBE
	■ PRESSURE RESISTANCE, LEAK TEST		
	● NUCLEAR HEAT BALANCE	● REACTOR NOISE ANALYSIS	
	● NUCLEAR HEAT BALANCE	● OFF-GAS MINITORING ■ SIPPING	■ BURN-UP ANALYSIS AND PERIODIC REPLACEMENT
COOLING WATER PURIFYING EQUIPMENT	● PRESSURE BRAKE	○ WATER CHEMISTRY DIAGNOSIS	

DIAGNOSIS PERIOD ● : DURING OPERATION ■ : DURING PERIODICAL INSPECTION
 ○ : DURING OPERATION □ : DURING PERIODICAL INSPECTION

FIG.17C

TABLE OF MAIN APPARATUS AND EQUIPMENT OF REACTOR

APPARATUS AND EQUIPMENT TO BE DIAGNOSED		MAIN FUNCTION
MOVABLE APPARATUS	RECIRCULATION PUMP	SUSTAINMENT OF RECIRCULATION FLOW RATE
	MAIN STEAM ISOLATION VALVE	EMERGENCY CUT-OFF OF STEAM FLOW
	MAIN STEAM SAFETY RELEASE VALVE	EMERGENCY PRESSURE RELEASE
	CONTROL ROD DRIVE UNIT	DRIVING AND EMERGENCY INSERTION OF CONTROL RODS
	ENGINEERING SAFETY DEVICE	EMERGENCY INJECTION OF HIGH-PRESSURE WATER INTO CORE
ELECTRIC INSTRUMENT / APPARATUS	IN-REACTOR NEUTRON MONITOR	MEASUREMENT OF NEUTRON FLUX DISTRIBUTION
	PROCESS MONITOR	MEASUREMENT OF TEMPERATURE, PRESSURE AND FLOW RATE
	REACTOR PROTECTING EQUIPMENT	SHUT-DOWN REACTOR UPON DETECTION OF ABNORMALITY
	RADIATION CONTROL EQUIPMENT	MEASUREMENT OF RADIOACTIVITY AND RADIOACTIVE RAYS

FIG.17D

TABLE OF METHODS FOR DIAGNOSING MAIN APPARATUS AND EQUIPMENT OF REACTOR

APPARATUS AND EQUIPMENT TO BE DIAGNOSED		DIAGNOSING METHOD		
		OPERATING PERFORMANCE	ABNORMAL SIGNS	MATERIAL DETERIORATION
MOVABLE APPARATUS	RECIRCULATION PUMP	● PRESSURE FLOW RATE MEASUREMENT	● VIBRATION MONITORING ● LOOSENED PART MONITORING ● UNMANNED CHECKING DEVICE	
	MAIN STEAM ISOLATION VALVE	● SURVEILLANCE TEST	■ OVERHAUL CHECK	
	MAIN STEAM SAFETY RELEASE VALVE	● SURVEILLANCE TEST	■ OVERHAUL CHECK	
	CONTROL ROD DRIVE UNIT	■ OPERATION TEST	■ OVERHAUL CHECK	
	ENGINEERING SAFETY DEVICE	● SURVEILLANCE TEST	■ OVERHAUL CHECK	
ELECTRIC INSTRUMENT / APPARATUS	IN-REACTOR NEUTRON MONITOR	● NUCLEAR HEAT BALANCE	● REACTOR NOISE ANALYSIS	■ BURN-UP ANALYSIS AND PERIODIC REPLACEMENT
	PROCESS MONITOR	● NUCLEAR HEAT BALANCE	● REACTOR NOISE ANALYSIS	
	REACTOR PROTECTING EQUIPMENT	● SURVEILLANCE TEST ■ PERIODIC CALIBRATION		
	RADIATION CONTROL EQUIPMENT	■ PERIODIC CALIBRATION		

DIAGNOSIS PERIOD ● : DURING OPERATION ■ : DURING PERIODICAL INSPECTION (ALREADY PRACTICED)

FIG. 18
TABLE OF MAIN SENSORS FOR DIAGNOSIS APPARATUS AND EQUIPMENT

DIAGNOSING SYSTEM	DIAGNOSING METHOD	MAINSENSORS
IN-SERVICE INSPECTION (ISI)	DEFECT SEARCH WITH ULTRASONIC WAVE	ELECTRON SCAN ULTRASONIC SENSOR
STEAM LEAK DETECTION	MEASUREMENT OF STEAM EJECTION NOISE	AE SENSOR, HIGH-SENSITIVITY MICROPHONE
LOOSENED PART MONITORING	MEASUREMENT OF CONTACT NOISE	HIGH-SENSITIVITY MICROPHONE
CORE NOISE ANALYSIS	EVALUATION OF APPARATUS VIBRATION FROM FLUCTUATIONS IN NEUTRON FLUX IN REACTOR	NEUTRON FLUX MONITOR
WATER CHEMISTRY DIAGNOSIS	DETECTION OF APPARATUS ABNORMALITY FROM CHANGES IN PLURAL WATER CHEMISTRY INDICES	DISSOLVED OXYGEN & HYDROGEN METER, CONDUCTIVITY METER, pH METER
MATERIAL DEGRADATION DIAGNOSIS	MEASUREMENT OF MINUTE MATERIAL CHANGES	SQUID, ATOM PROBE

PLANT MONITORING AND DIAGNOSING METHOD AND SYSTEM, AS WELL AS PLANT EQUIPPED WITH THE SYSTEM

CONTINUATION STATEMENT

This application is a continuation of application Ser. No. 08/247,039 filed on May 20, 1994, now U.S. Pat. No. 5,623,109.

BACKGROUND OF THE INVENTION

The present invention relates to monitoring and diagnosing method and system which monitor and diagnose the condition and operation of plants such as nuclear power plants and thermoelectric power plants.

There are various kinds of plants for producing energy and reaction products, e.g., nuclear power plants using boiling water reactors and pressurized water reactors, thermoelectric power plants in which petroleum, coal, natural gas, etc. are burnt, and chemical plants for producing and refining petrochemicals such as ethylene (hereinafter these different types of plants referred to simply together as plants). In these plants, objects to be controlled are subject to a wide temperature range from low to high temperatures, and phase of the objects is changed from liquid to gas phase and, in some cases, even to solid phase at different locations within each plant.

For each condition of start-up, steady operation and shutdown of a plant, the temperature and phase of the controlled object are variously changed at different locations within the plant. Generally, the operation of a plant is controlled by a computer. In order to achieve optimum operation efficiency of the plant or smooth start-up and shutdown thereof, various variables in the plant such as pressure and temperature are measured every moment, and the plant is operated under control of the computer so that the various variables are optimized.

FIG. 16 is a schematic structural view of main apparatus and equipment of a nuclear power plant using a boiling water reactor.

In FIG. 16, reactor internals such as a fuel assembly and a jet pump 22 are disposed in a pressure vessel 17. The pressure vessel 17 is housed in a reactor containment vessel 16 along with other main apparatus and equipment for controlling and cooling the reactor, such as a control rod drive unit and a recirculating pump motor 29.

During normal operation, control rods are withdrawn from a core 23 so that nuclear fission of uranium occurs as the fuel reaches critical mass to produce heat. The jet pump 22 is driven by the recirculation pump motor 29 disposed in a recirculation loop 26, whereby cooling water is circulated to remove the heat generated by the nuclear fission from the core. Then, high-pressure steam at 280° C. and 6.9 MPa is produced and supplied to a turbine through a main steam line 24 for driving the turbine to thereby generate electricity. The steam is condensed by a condenser into water that is returned to the reactor through a feed-water line 25. During the operation, nitrogen gas is filled into the reactor containment vessel 16 for the purpose of non-combustibility.

If any abnormality should occur in the reactor system, the reactor containment vessel 16 is isolated by operating main steam isolation valves installed inside and outside of the reactor containment vessel 16. Also, any overpressure in the reactor is relieved through a safety release valve 18, and safety equipment such as emergency core cooling system is operated.

Denoted by reference numeral 21 is a shroud disposed to surround the core 23. Further, 20 is a steamy water separator, 37 is a dry well, and 19 is a steam drier. The steam water separator 20 serves to remove condensed water, and the dry well 37 serves to release a steam/water mixture in the event of a loss-of-coolant accident. 28 is a coolant purifying pump which supplies a coolant to the feed-water line 25 through a filter/demineralizer 27. 15 is a reactor containment vessel spray for scattering cooling water, and 30 is a similar spray. 31 is a turbine pump for cooling in the event of isolation. In case of the reactor isolated from the turbine system, the pump 31 serves to cool the reactor.

Further, 32 is a residual heat removal unit and 36 is a residual heat removal pump, the heat exchanger 32 and the pump 36 serving to remove the decay heat after shutdown of the reactor. 33 is a high-pressure core spray pump, 34 is a low-pressure core spray pump, and 35 is a pressure suppression chamber.

In the above-described nuclear power plant, the operation of the nuclear power plant is periodically shut down and the main equipment and apparatus are dismantled and disassembled to check for the presence or absence of an abnormality and any degree of deterioration for the purpose of ensuring reliability of the nuclear power plant. Also, the presence or absence of an abnormality is checked in a nondestructive manner and, if any abnormality is found, the relevant apparatus and/or parts are repaired or replaced with new ones, thereby ensuring the reliability in the operation of the nuclear power plant. In the nuclear power plant during the operation, the operating condition represented by parameters primarily related to the reactor, such as power, temperature, pressure and flow rate of circulating water, are monitored at all times. Based on the monitored results, it is confirmed that the operating condition of the nuclear power plant is normal. For each of the pumps and other main components, such parameters as rotational speed, delivery pressure, and temperature and flow rate are monitored to confirm the operating condition thereof. In addition, not only the vibrations and temperature of each apparatus, but also leaked steam, water, radioactive rays, etc. around the apparatus are monitored to confirm that the environment surrounding the apparatus is normal. Thus, the presence or absence of an abnormality in the operation of the nuclear power plant is always confirmed.

For periodic inspection of the equipment and apparatus, the advanced checking operation is promptly performed by expert workers having advanced skills in conformity with legal check items. FIG. 17A-17D is a table showing a summary of methods for diagnosing the main apparatus and equipment, and FIG. 18 is a table of main sensors for diagnosis of the main apparatus and equipment (reference: "Equipment Diagnosing System of Nuclear Power Plants", Uchida and three others, Sensor Technology, October 1992, pp. 84-89).

As the prior art relating to monitoring and diagnosis of plants and apparatus, there are known, for example, patent laid-open publications concerned with apparatus (JP, A, 58-134312 and JP, A, 3-220498) and with plants (JP, A, 58-215593, JP, A, 63-313208 and JP, A, 63-241876). In these publications, a prediction model for the operation of an apparatus or plant to be monitored is utilized to detect an abnormality from the difference between the model and actually observed results.

SUMMARY OF THE INVENTION

Meanwhile, it has been recently desired to improve reliability of plants such as nuclear power plants and to increase

an availability factor of plants by simplification of the periodic inspection.

There is a fear in the future that as plants such as nuclear power plants are aged year by year, the occurrence of troubles due to deterioration of apparatus and materials over time will lower the reliability of the plant. Also, it is expected that the number of expert workers necessary for the periodic inspection of the plant will be insufficient. It will therefore be necessary to efficiently predict a possibility of the occurrence of an abnormality in apparatus and materials with high reliability during the operation of the plant. It is also required to sense an abnormality of apparatus and so on in the very early stage.

Accordingly, there is a demand for accurate and automatic monitoring and diagnosis of plant equipment which can suppress a reduction in reliability of plants due to deterioration of apparatus and materials over time, can suppress a reduction in the availability factor due to the periodic inspection, and can exactly grasp time-dependent characteristics of plants.

To improve reliability in monitoring and diagnosing highly complicated facilities such as nuclear power plants, for example, a function of exactly analyzing and diagnosing an abnormality, taking into account the personality of each plant including its production record, check/repair record and operation record, is indispensable. In addition, not only a function of processing the data to promptly and surely analyze many kinds of and a large number of monitored data and detect an abnormality, but also a function of surely transmitting the result of diagnosis and the measures to be dealt with to operators are also necessary. Then, an overall monitoring and diagnosing system in which the analyzing and diagnosing functions and the transmitting function are coupled to each other is desired.

In the above-described prior art, however, a monitoring and diagnosing method which can exactly analyze and diagnose an abnormality, taking into account the personality of a plant, including its production record, check/repair record and operation record, has not yet been realized.

Accordingly, an object of the present invention is to realize a plant monitoring and diagnosing method and system which can exactly analyze and diagnose an abnormality with high reliability, taking into account the production record, the check/repair record, the operation record, etc. of a plant, and can simplify the periodic inspection to increase an availability factor of the plant.

To achieve the above object, the present invention is arranged as follows.

In a plant monitoring and diagnosing method, detecting and accumulating plant operating conditions, apparatus operating conditions and environment conditions, inputting and accumulating plant inspection data, and monitoring and diagnosing plant conditions based on plant record information including the accumulated detection data and inspection data.

In the above plant monitoring and diagnosing method, preferably, the plant record information is stored in the form of a plant chart in which the detection data and the inspection data are compressed and accumulated such as a personal clinical chart, and the plant conditions are diagnosed based on the data in the plant chart.

In the above plant monitoring and diagnosing method, preferably, current plant conditions are predicted in accordance with the data in the plant chart and a plant condition predicting model, and an abnormality in the plant conditions are monitored and diagnosed based on a comparison

between the predicted current plant conditions and the current detection data.

Also, in the above plant monitoring and diagnosing method, preferably, when an abnormality is detected as a result of diagnosing the plant conditions, an abnormal location and an abnormal item are identified and events which will ensue from the abnormality are predicted.

In the above plant monitoring and diagnosing method, preferably, the identified abnormal location and item and the event incidental to the abnormality are indicated by display means.

Further, in the above plant monitoring and diagnosing method, preferably, a residual life for each plant component, apparatus and member is evaluated based on the data in the plant chart and material degradation data calculated from the chart data.

In a plant monitoring and diagnosing system, the system comprises first input means for receiving detection data of plant operating conditions, apparatus operating conditions and environment conditions, second input means for receiving plant inspection data, first input data processing means for preparing data for use in plant monitoring and diagnosis based on the detection data from the first input means, second input data processing means for preparing data for use in plant monitoring and diagnosis based on the inspection data from the second input means, a plant chart for storing the data prepared by the first and second input data processing means, and monitoring and diagnosing means for monitoring and diagnosing the plant conditions based on the data stored in the plant chart.

In the above plant monitoring and diagnosing system, preferably, the monitoring and diagnosing means includes abnormality diagnosing means for diagnosing a plant abnormality based on the data from the plant chart and the data from the first input data processing means.

Also, in the above plant monitoring and diagnosing system, preferably, the abnormality diagnosing means diagnoses an abnormality in the plant operating conditions and the plant apparatus operating conditions.

Further, in the above plant monitoring and diagnosing system, preferably, the abnormality diagnosing means identifies an abnormal plant location and an abnormal item and predicts ensuring events.

Preferably, the above plant monitoring and diagnosing system further comprises display means for displaying the abnormal location, the abnormal item and the ensuring events identified and predicted by the abnormality diagnosing means.

Also, in the above plant monitoring and diagnosing system, preferably, the abnormality diagnosing means selects a countermeasure for dealing with the location and details of the abnormality, and the display means displays the selected countermeasure.

In the plant monitoring and diagnosing method, plant operating conditions, apparatus operating conditions and environment conditions are detected and accumulated, and detection data are inputted and accumulated. The accumulated detection data and inspection data are stored as plant record information. The plant conditions are monitored and diagnosed based on the plant record information. Therefore, when the record information shows detection of abnormal signs or the like in the past, for example, the monitoring and diagnosis are performed in consideration of the past data even if the current condition is sound. When an abnormality is detected, the location and details of the abnormality are

identified and the ensuing events are predicted. In the plant monitoring and diagnosing system, plant operating conditions, apparatus operating conditions and environment conditions are input through first input means. Also, inspection data are input through second input means.

Data for use in plant monitoring and diagnosis are prepared by first and second data processing means based on the detection data from the first and second input means. The data prepared by the first and second data processing means are stored in a plant chart. Then, the plant conditions are diagnosed by monitoring and diagnosing means based on the data stored in the plant chart.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram for explaining the operation of a plant monitoring and diagnosing method according to one embodiment of the present invention.

FIG. 2 is a schematic structural view of a nuclear reactor system to which the present invention is applied.

FIG. 3 is a table showing a diagnosis flow for a recirculation pump.

FIG. 4 is a graph showing one example of preserved data for the recirculation pump as a part of the plant chart.

FIG. 5 is a table showing a thermal power diagnosis flow for a large-scaled plant.

FIG. 6A is a graph showing one example of preserved data for the thermal power diagnosis as a part of the plant chart.

FIG. 6B is a graph showing one example of preserved data for the thermal power diagnosis as a part of the plant chart.

FIG. 7 is a block diagram of an entire plant monitoring and diagnosing apparatus according to one embodiment of the present invention.

FIG. 8 is a block diagram of the monitoring and diagnosing system in the embodiment of FIG. 7.

FIG. 9 is a block diagram of another example of the monitoring and diagnosing system.

FIG. 10 is a block diagram of still another example of the monitoring and diagnosing system.

FIG. 11 is a block diagram of an entire plant monitoring and diagnosing apparatus according to another embodiment of the present invention.

FIG. 12 is a block diagram of an operation planning system in the embodiment of FIG. 11.

FIG. 13 is a diagram for explaining details of the embodiment of FIG. 8.

FIG. 14 is a block diagram of a plant monitoring and diagnosing apparatus according to still another embodiment of the present invention.

FIGS. 15A, 15B and 15C are successive illustrations showing details of the embodiment of FIG. 14.

FIG. 16 is a schematic structural view of a boiling-water reactor power plant.

FIG. 17A is a table of main apparatus and equipment of a reactor.

FIG. 17B is a table of methods for diagnosing main apparatus and equipment of a reactor.

FIG. 17C is a table of main apparatus and equipment of a reactor.

FIG. 17D is a table of methods for diagnosing main apparatus and equipment of a reactor.

FIG. 18 is a table of main sensors for diagnosis of apparatus and equipment of a reactor.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 is a block diagram for explaining the operation of a plant monitoring and diagnosing method according to one embodiment of the present invention.

In FIG. 1, taking a nuclear power plant as an example, information about an operating condition 1 of the nuclear power plant, an operating condition 2 of each of component apparatus, environment 3, etc. is detected by respective detection means and accumulated in appropriate storage means every moment through an on-line monitor 6. These data are combined and brought together into a set of plant status variables 8. Water chemistry information 4 about cooling water represented by radioactivity and chemical parameters such as dissolved oxygen concentration, pH, conductivity, metal ions, various anions and suspended substances, is detected by respective chemical and radiation (α , β , γ -ray) analysis through the on-line monitor 6 for part of the information, but through an off-line monitor 7 for most thereof.

The set of plant status variables 8 is exchanged and updated to new data every moment. Past data of the set of plant status variables 8 are accumulated in the storage means as a set of past plant status variables 9. Further, inspection information 5 resulted from an overhaul during the periodical inspection of the nuclear power plant and water quality/chemical information 4 measured by the off-line monitor 7 are also accumulated in the set of past plant status variables 9.

The set of past plant status variables 9 is put together (compressed) into a plant chart 11 and preserved as well as a personal clinical chart. For nuclear power plants, there are models for predicting various conditions of the plant. These models are employed to predict the current condition of the plant based on the past plant data. While the prediction using the models is usually performed based on the plant design data, a status variable prediction 2 in FIG. 1 is performed based on the plant chart 11, i.e., in consideration of the personality of the plant.

Data A represented by the set of plant status variables (current) 8 and data B represented by the set of plant status variables (predicted current values) 10 are compared with each other by comparison means 100. If the equation $A-B \leq \epsilon R$, which indicates the deviation between the data A and B within a certain range of error R, is not satisfied, the plant is diagnosed as abnormal condition 100A. If the equation $A-B \leq \epsilon R$ is satisfied, it is determined by the comparison means 101 whether the data A is within the allowable area (AL \leq A \leq AH) or not. Notice that AL is the lower allowable limit and AH is the upper one. If the value of data A is within the allowable range, then the plant is diagnosed as normal condition 101B. If the value of data A is outside the allowable range, then the plant is diagnosed as abnormal condition 101A.

When the plant is diagnosed as including an abnormality, the abnormal apparatus and factor are identified by detailed collation between the data A and B, analysis of the plant chart, and evaluation based on the prediction models. Also, events which might ensue from the abnormality are predicted using the models to clarify the time frame until the countermeasure such as shut-down of the plant or check, repair or replacement of the apparatus should be taken, thereby making it possible to take systematic actions (as indicated by 14).

More specifically, in addition the characteristic relating to the generation of energy, i.e., the intrinsic purpose of the

plant, the relationship among number of revolution, delivery pressure and flow rate of each pump, the relationship between positions of control rods and power, and the correlation among fluctuations in vibration and number of revolution of each pump, temperature fluctuations and power fluctuations are analyzed to evaluate and diagnose whether the abnormality is attributable to change in any characteristic of the individual apparatus or change in the plant characteristics. Whether the operating conditions of each of the apparatus and locations is proper or not is checked to diagnose a characteristic deterioration or abnormality for each apparatus and detect abnormal signs. Further, the information about the operating conditions of the individual apparatus is promptly collected and combined mutually to diagnose them for earlier discovery of an abnormality, provide a highly reliable data base, and to prepare the chart of the plant condition automatically.

Such collection and evaluation of the plant data are not limited to for the objects under control of a computer. Information about the operating conditions of all the plant apparatus and information about the specification and inspection data of each apparatus are collected to a central control room or the like and are combined with the operation record and mode of the plant, thereby synthesizing the information.

A description will now be made of the case where the present invention is applied to a nuclear reactor system.

FIG. 2 shows main measuring elements for use in the nuclear reactor system. In FIG. 2, the nuclear reactor system comprises a core A2 made up of fuel assembly in a reactor pressure vessel A1, and a control rod A3 and a control rod drive unit A4 for adjusting reactivity of the core and controlling a power. The nuclear reactor system further comprises a recirculation pump A5, a jet pump 6 and a recirculation system A7 for circulating cooling water through the core to cool the core and take thermal energy as steam out of the core, and a turbine A8 and an electric generator A9 for converting thermal energy of the steam generated in the core into electric energy.

Further, the nuclear reactor system comprises a main steam system A10 for introducing the steam to the turbine A8, a condenser A11 for condensing the steam discharged from the turbine A8, and a feed-water system A12 for reinjecting the cooling water, which has been returned to water again in the condenser A11, to the reactor. Incidentally, A14 is a drier and A15 is a separator.

The most important parameter indicating the reactor condition is a power of the reactor. The reactor power is usually represented by an electric generating power and a thermal power. While the power directly produced from the reactor is in the form of heat, the reactor power is generally obtained in the form of electric energy for the purpose of generating electricity. In usual BWR power plants, the heat efficiency is slightly fluctuated depending upon, e.g., the temperature of sea water introduced to the condenser, but is approximately 33.3% with the definite correlation existing between the electric generating power and the thermal power. It is generally thought that when the electric generating power is fluctuated, this is resulted from fluctuations in the thermal power.

Gross measurement of the reactor thermal powers is made based on the temperature, pressure and flow rate of the main steam. The enthalpy is calculated from the temperature and the pressure, and is then multiplied by the flow rate to calculate the total enthalpy. Since the reactor power is originally produced by nuclear fission in the reactor, the

thermal power can also be calculated from a fission rate. Thus, in-reactor fluctuations in distribution of the neutron flux and distribution of the fission rate during the operation of the reactor are calculated every moment through nuclear physical calculations for the reactor. A neutron flux monitor A13 disposed in or around the reactor always monitors the neutron flux, and the measured value is used to calibrate the above fluctuation values, whereby the in-core fission rate and the thermal power are calculated with high accuracy. Thus, the thermal power of the reactor is calculated from the neutron measurement.

The thermal power obtained from the neutral measurement (hereinafter referred to as nuclear thermal power) must be coincident with the thermal power calculated from the aforementioned enthalpy of the main steam (hereinafter referred to as macroscopic thermal power). If both the powers do not coincide with each other, this means that an error is caused in the nuclear thermal power or the macroscopic thermal power due to an abnormality or the like in the measuring unit. It is therefore required to find the cause of the error and to obviate the cause by third parameter for checking which of the nuclear thermal power and the macroscopic thermal power is proper is the aforementioned electric generating power. When two of the three powers (i.e., the nuclear thermal power, the macroscopic thermal power and the electric generating power) coincide with each other, the remaining one is abnormal.

In the case of the reactor, the core reactivity is changed with the operation time. With the elapse of the operation time, there proceeds nuclear fission of U-235 in the fuel assembly loaded in the core. As a result, the fuel assembly are consumed and the fission products produced by the nuclear fission absorb neutrons, whereupon the reactivity is lowered. On the other hand, the reactivity is also lowered not only upon withdrawal of the control rod inserted to the core, but also upon an increase in the flow rate circulated. When the flow rate is increased, the flow rate per power is reduced and the average coolant temperature in the core is lowered, thereby reducing a void fraction in the core. Since BWR has a negative void factor, the reactor power is increased with a reduction in the void fraction. The reduction in the void fraction is also caused with an increase in the flow rate through the feed-water system.

Thus, the thermal power of the reactor is changed upon burn-up of the fuel, withdrawal/insertion of the control rod, an increase/decrease in the flow rate circulated, and an increase/decrease in the flow rate of the feed water. The change rate depends on the design and personality of the plant. In practice, plants are different in their personality even with the same design because of errors in manufacture of each plant. With due consideration paid to the personality of the plant, the thermal power of the reactor can be estimated from the position of the control rod inserted if the flow rate circulated remains the same, or from variations in the flow rate circulated if the position of the control rod inserted remains the same. The thermal power of the reactor thus estimated is also compared with the aforementioned nuclear thermal power, macroscopic thermal power and electric generating power to check the normal operating condition of the reactor from the viewpoint of balance of the entire plant.

To evaluate the plant balance, characteristic changes in the individual component apparatus are indispensable. FIG. 3 shows one example of a diagnosis flow and a chart of the recirculation pump. More specifically, measurement items include measurement of the amount of dissolved metal ions, measurement of the number of valve revolutions, measure-

ment of the pump current and voltage, measurement of the pump rotational speed, measurement of the difference pressure across an orifice, and measurement of the acceleration. Information obtained from the measurement items includes valve sheet wear information from the measurement of the amount of dissolved metal ions, valve opening information from the measurement of the number of valve revolutions, power load information from the measurement of the pump current and voltage, flow rate information from each of the measurement of the pump rotational speed and the measurement of the difference pressure across an orifice, and vibration information from the measurement of the acceleration. Then, correlation evaluating data are created from the valve sheet wear information, the valve opening information, the power load information, the flow rate information, and the vibration information. These correlation evaluating data are accumulated as a pump chart.

The flow rate recirculated is variable upon change in the number of revolutions of the recirculation pump A5. By calculating the flow rate from the number of revolutions and measuring the flow rate directly from a flow meter, the correlation between the number of revolutions and the flow rate due to fluctuations in the pressure loss in the entire recirculation system is calibrated every moment. These data of the number of revolutions and the flow rate are separately measured in an automatic manner and are preserved as plant data primarily in the form of chart paper. To preserve such raw data as the flow rate data is itself important. However, if those data are preserved as separate data, the data volume stored becomes so large that it is difficult to immediately take out the corresponding data when a check is required upon the occurrence of trouble in some day.

Therefore, the data of the number of revolutions and the flow rate are put together into time-dependent correlation data of both the number of revolutions and the flow rate immediately after the sampling, as shown in FIG. 4, the correlation data being preserved as a chart of the recirculation pump A5. This makes it possible to grasp the pump characteristics and to diagnose an abnormality of the pump. More specifically, in FIG. 4, the vertical axis represents the flow rate $Y(t)$ and the horizontal axis represents the number of revolution $X(t)$. The time-dependent correlation data between the number of revolutions and the flow rate, as shown, is preserved in a storage. In the correlation analysis therebetween, if a plotted point deviates 10% or more from the correlation specific to the plant, it is judged that any abnormality exists. Such abnormality diagnosis can be used for future estimation of the pump characteristics so that the time at which the abnormality will exceed the allowable characteristic range may be predicted to schedule repair or replacement of the pump till that time.

In addition to the correlation between the number of revolutions and the flow rate, the power consumption, vibrations, noise and valve related data are also included in the chart of the recirculation pump for enabling even slight variations to be evaluated based on a plurality of parameters. Specifically, vibrations are generated in various ways, e.g., in transient states of the number of revolutions and the flow rate, at the number of revolutions and the flow rate above certain values, and after a certain time regardless of the number of revolutions and the flow rate. For the vibration generated regardless of the number of revolutions and the flow rate, it is also required to check reliability of the vibration system itself. For the vibration generated at the number of revolutions and the flow rate above certain values, the correlation among the number of revolution, the number of vibrations and the magnitude is analyzed and, if

a significant correlation is found, the pump is diagnosed as having an abnormality in relation to its rotation.

FIGS. 5 and 6 shows one example of a chart for large-scaled plant. As to the reactor thermal power, a described above, there are;

- (1) thermal power estimated from the electric generating power (voltage and current of the generator),
- (2) thermal power estimated from characteristics (temperature, pressure and flow rate) of the main steam,
- (3) thermal power estimated from the neutron flux measured value (nuclear fission rate), and
- (4) thermal power estimated from the position of the control rod inserted, the flow rate recirculated, and feed-water characteristics (feed-water temperature and flow rate).

The correlation among these thermal powers (1) to (4) is determined every moment and is put together into a function of the elapsed time or a function of any one of the four thermal powers (1) to (4). In theory, the four thermal powers (1) to (4) should coincide with one another. But even if the respective data have no intrinsic errors, it is usual that the four thermal powers (1) to (4) do not exactly coincide with one another. Whether the individual thermal powers are proper or not is confirmed by checking the data from which the thermal powers are derived and, thereafter, the compressed data are stored as data having been evaluated in the form of a time-dependent function, as shown in FIG. 6(A). In other words, the data of the thermal powers (1) to (4) are stored in the form of a graph in which the vertical axis represents thermal power and the horizontal axis represents the time.

By carefully evaluating whether the shifts between the four thermal powers are changed or not over time and whether the shifts between the four thermal powers are changed or not at the same thermal power, it is possible to find a slight characteristic deterioration of the apparatus (as illustrated in FIG. 6(B)) which can not be judged from only one of the thermal powers.

When the value of the thermal power (4) is significantly larger than the values of the other thermal powers (1) to (3), any of the following events can be thought as a possible reason:

- (a) the actual control rod position is shifted from the indicated value toward the withdrawal side,
- (b) the control rod poison is deteriorated,
- (c) the jet pump efficiency is lowered, or
- (d) the fuel reactivity is lowered with an iron crud abnormally adhering to the fuel surface.

The characteristics of the recirculation pump can be confirmed by the above checks. The temperature and flow rate of the feed-water can also be cross-checked, i.e., confirmed by detailed reviews from various angles.

The above events of (a) false indication of the control rod position and (b) poison deterioration can be confirmed by inserting the relevant control rod and withdrawing the other plural control rods one at a time. The above event of (c) lowering of the jet pump efficiency is difficult to check on-line, but a reduction in smoothness of the nozzle inner surface due to deposition of an iron crud onto the nozzle portion, which is thought as one of factors responsible for the efficiency reduction, can be analytically estimated from time-dependent data of the iron crud concentration in the feed-water and the recirculated water. A nozzle clearance failure, block-off by a loosened part, and so on are confirmed by overhaul inspection.

The above event of (d) fuel contamination can also be evaluated from analysis of the iron crud concentration in the reactor water. A set of multi-item data relating to the above

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(1) to (4) are referred to as a power data pattern. Analysis on time-dependent variations of this pattern is expected to achieve more prompt diagnosis than analysis and evaluation tracing back to the individual original data. In addition, the volume of data to be stored can be reduced. From comprehensive judgement based on the accuracy in measuring the reactor thermal power, the accuracy in calculating the reactor reactivity, the accuracy in measuring the neutron flux and so on, it is appropriate that a decision criterion for determining an abnormality is set to the time at which the measured data deviates or will possibly deviate 1% or more from correlation specific to the plant.

By comparing the chart with the above plant condition data and carrying out automatic diagnosis using an expert system in parallel, it is possible to promptly detect abnormal signs identify the abnormal factor with high reliability under flexible adaptation to changes in the characteristics of the plant itself every moment.

Generally, reliability of apparatus and materials used in a plant tend to lower over time. Since the amount of information and reliability of a chart indicating the plant characteristics are increased and improved with the elapse of the plant operation time, the diagnosis accuracy is improved with an increase in the operation time and hence is complementarily to reliability of apparatus and materials that is lowered with an increase in the operation time.

Furthermore, it is possible not only to inform plant operators of the presence or absence of an abnormality and the abnormal factor in an easily apprehensible manner, but also to promptly and exactly present the gravity of the occasion to the operators by quantitatively predicting incidental events which might occur if the abnormality spreads and then displaying them on the CRT screen.

Additionally, as a result of the prompt and highly reliable detection of abnormal signs and identification of the abnormal factor, the number of equipment and systems subject to the periodical inspection can be reduced, and the equipment and systems to be newly subject to the periodical inspection can be automatically picked up based on the detected deterioration signs.

When displaying the predicted results of the events incidental to the abnormality, the predicted events can be indicated on a display in the form of graphs of related physical variables or moving pictures visually representing the events themselves. This makes it possible for plant operators to more promptly and exactly grasp the occasion in visual way, and to prevent the occurrence of a trouble, such as escalation of the abnormal condition, due to erroneous judgment of the plant operators. By simultaneously displaying selectable measures to deal with the occasion and results of the measures, it is possible to support selection of the appropriate measure and to create a wide margin for the subsequent measure. The selection of the measure can be made while confirming various situations of the plant on the display.

Moreover, by installing another display in, for example, a monitoring center for monitoring operating situations of plural plants other than the central control room of the relevant plant, the countermeasure can be selected with the aid of judgement by many other concerned people and experts. As a result, even such an abnormal event as not expected can be exactly dealt with after grasping event more closely.

The plant chart contains the data specific to the plant, i.e., corresponding to the personality of the plant, and exact abnormal diagnosis is enabled depending upon each of plants having different records in production, operation and

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repair by utilizing the plant art. By additionally storing trouble occasions in other plants as reference data in the plant chart, those reference data contribute to assisting estimation of the cause of an abnormality and selection of the countermeasure, and to further improving reliability of the abnormality diagnosing system.

FIGS. 7 and 8 are block diagrams of a monitoring and diagnosing apparatus according to another embodiment of the present invention.

Referring to FIG. 7, monitored data from a plant 60 are taken in by a monitoring and diagnosing system 61 including the plant chart 11, and the diagnosis result based on the plant chart 11 is transmitted to an operation/control system 62 for operating and controlling the plant 60. The plant 60, the monitoring and diagnosing system 61, and the operation/control system 62 cooperatively make up a plant in the broad aspect and are all installed in the same site.

FIG. 8 is a block diagram of the monitoring and diagnosing system 61. In FIG. 8, the plant condition monitoring data from the plant 60 are taken in by a monitoring system 64 utilizing various sensors, monitors, etc. and are subject to data processing such as correlation analysis, if necessary. The monitored data thus processed to be suitable for diagnosis are taken in by an abnormality diagnosing system 45, a condition predicting system 65 and the plant chart.

Supplied to the plant chart 11 are record information such as about the plant operating condition and the apparatus operating condition through the monitoring system 64, and the inspection results and engineering conditions through an inspection system 66. Then, characteristics specific to the plant, representing the personality of the plant, are accumulated in the plant chart 11 as various kinds of data. Supplied to the abnormality diagnosing system 45 are current operating condition data of the plant or apparatus obtained directly as the monitored data, condition data predicted from the monitored data to be so by the condition predicting system 65 in which prediction models are incorporated, and the plant personality data written in the plant chart 11. Then, the abnormality diagnosing system 45 diagnoses the plant condition based on the operating condition data, the expected condition data, and the personality data.

Further, the data of the plant chart 11 and material degradations quantitated by a degradation evaluating system 46 from the chart data are taken in by a residual life evaluating system 47 which calculated the residual life for each of the apparatus and members using models adapted to analyze the deterioration of the material strength and behavior of the crack propagation. The diagnosis and evaluation results by the abnormality diagnosing system 45 and the residual life evaluating system 45 are both supplied to the plant chart 11 as update data. The data from the abnormality diagnosing system 45 and the residual life evaluating system 47 also provide operation/control information. Further, the data from the residual life evaluating system 47 provide security program information.

The abnormality diagnosing system 45 may be arranged such that the weights are allocated depending upon importance of objects to be monitored, such as various apparatus, to diagnoses them in the order of the weights. In this case, it is possible to change the weights depending the result of abnormal diagnosis and to supply the changed data to the plant chart 11 as update data.

FIGS. 9 and 10 show another example of the monitoring and diagnosing system. In FIG. 9, an abnormality monitoring and diagnosing system 68 comprises the monitoring system 64, the inspection system 66, the condition predicting system 65, the plant chart 11, and the abnormality

diagnosing system 45. In FIG. 10, a life monitoring and diagnosing system 69 comprises the monitoring system 65, the inspection system 66, the degradation evaluating system 45, the plant chart 11, and the residual life evaluating system 45.

By using the abnormality monitoring and diagnosing system 68 or the life monitoring and diagnosing system 69, shown respectively in FIGS. 9 and 10, as one kind of the monitoring and diagnosing system, the system size can be reduced corresponding to the limited functions. On the other hand, the arrangement of FIG. 8 in which the abnormality monitoring and diagnosing system 68 and the life monitoring and diagnosing system 69 are combined with each other has an advantage of filling up the plant chart 11 to support reliability of the diagnosis result because of the combined systems.

Furthermore, as shown in FIG. 11, an operation planning system 63 can be added to the arrangement shown in FIG. 7. The operation planning system 63 takes in the result of the residual life evaluation from the monitoring and diagnosing system 61, prepares a plant security program and a plant operation program based there, and supplies the programs to the operation/control system 62. In the operation planning system 63, as shown in FIG. 12, the result of the residual life evaluation from the monitoring and diagnosing system 61 data from other plants relating to attainment of personals and materials necessary for the security program and the security operation are supplied to a security program system 60 which prepares the security program based on the supplied result and data. Further, an operation program system 71 prepares the operation program using the security program, operation programs of the other plants, and data relating to predicted demand for the plant product, followed by feeding it back to the operation/control system 62.

In FIG. 11, the operation planning system 63 serves to determine countermeasures for a relatively long term. The operation planning system 63 and the residual life evaluating system 47 as part of the monitoring and diagnosing system 61 are not necessarily included in the aforementioned plant of the broad aspect (i.e., installed in the same site as the plant 60), and may be installed in a different place as a facility for handling the operation planning control and the security program.

The arrangement of FIG. 8 will be described in more detail with reference to FIG. 13. Note that the same apparatus, members and so on in embodiments of FIGS. 1 and 8 are denoted by the same reference numerals.

In FIG. 13, data such as material, performance and specification data 37 and engineering condition data 38 or apparatus/members, which were installed during construction of the plant, during inspection such as the periodical inspection and during repair/replacement, are input through a terminal 41 of a chart data processor 44 for preparing and sustaining the plant chart 11. The data input during inspection are entered as numerical values for, e.g., constituent elements of materials which can be represented by numerical values, and as codes for attributes such as material names which can not be quantitated. The engineering condition data 38, e.g., the welding condition and so on, are also input in accordance with the set code.

In addition to key entry through a keyboard, data may be input from a recording medium such as a card by using an optical or magnetic code reader 40. By marking respective codes in parts of surfaces of apparatus/members by such means as engraving or printing and inputting those codes using the code reading directly from the apparatus/members themselves as recording media, it is possible to prevent a

trouble caused by an accidental missing or mix-up of the recording medium, and to carry out data entry itself quickly and surely. In case of a nuclear power plant, the above method provides the advantages that the possible problems of leaving cards or the like in the reactor or increasing contaminants which may be caused with operators carrying the cards into the reactor can be avoided and radiation exposure can be reduced by a shutdown of the working time. Through the above process, a portion of the plant chart 11 relating to the specification data, etc. of the apparatus/members is automatically update.

On the other hand, current monitored values of plant operating condition data 1, apparatus operating condition data 2, and in-plant environment data 3 including water quality data 4, as well as trends of the past monitored values thereof are processed by a data processor 43 for monitoring through an on-line monitor 6, and off-line monitor 7 and a process computer 39 to be automatically taken into the plant chart 11. The data taken into the plant chart 11 are not always the monitored signals themselves, but the plural kinds of monitored signals are subject to data processing, such as regression analysis, correlation analysis and frequency analysis, for conversion into advanced monitoring information signals which are then taken into the plant chart 11. This serves to achieve data compression and to increase sensitivity of the monitoring.

Based on the data of the plant chart 11 updated upon occasion and the past and current plan operating condition data obtained from the monitoring system, main factors (material properties, stress and environment) of material deterioration are quantitated in a degradation evaluating system 46. In the case of a nuclear power plant, material properties at the time of installation (or inspection) are evaluated from both the chart data of material properties and compositions of the apparatus/members before the installation (or inspection) and the chart data of engineering conditions such as welding in accordance with an evaluation model prepared beforehand. Further, using the chart data of the plant operating condition such as time-dependent variations in a neutron flux distribution, current and future changes in the material properties such as radiation embrittlement and radiation induced segregation are evaluated in accordance with an evaluation model also prepared beforehand. From the future changes in the material properties, the time of the next periodic inspection, the time of the periodic inspection after the next, etc. are evaluated.

Likewise, as to stress, the residual stress at the time of the installation (or inspection) is evaluated from both the charge data of material machining and the chart data of the engineering conditions. Then, using the chart data of the plant operating condition, relaxation and generation of the stress, fluid induced vibration, the thermal stress through the plant operation, etc. are evaluated. As to environment, the radical concentration, the corrosion potential, etc. are evaluated primarily from the current monitored data of the plant operating condition using an evaluation model also prepared beforehand. In the residual life evaluating system 47 which receives the thus-quantitated material degradations as input parameters, crack generation, joining and progress behavior 471 and strength deterioration behavior 472 are analyzed by a residual life evaluating section 473 to predict the remaining lives of the apparatus/members.

Based on the prediction result of the residual life evaluating section 473, a countermeasure selecting section 474 prepares a preventive maintenance program. When the remaining lives predicted in consideration of a safety factor with errors in the various chart data and various evaluation

and analysis models taken into account exceed the design lives of the apparatus/members, the security program is not required to be corrected. However, if the predicted residual life is shorter than the design life, the residual life evaluating system 47 selects an optimum preventive maintenance process among from various maintenance processes, such as material properties improvement and stress relaxation by repair/replacement and environmental mitigation, in view of safety and economy. In this case, it is not always required to prolong the predicted residual life up to the design life by only one kind of security engineering process. For example, if hydrogen is first injected to mitigate the corrosive environment in the plant and the repair/replacement is performed in the next periodic inspection, it is possible to avoid shutdown of the plant other than scheduled and to achieve stable supply of electric power.

As to the apparatus/members for use in the repair/replacement, by recording chart information in the form of codes on recording media such as cards beforehand and storing them to provide for preventive maintenance, the recorded information can be utilized as one kind of data base for prompt and proper selection of the optimum engineering process in case of accidental trouble. It is sufficient to perform the residual life evaluation at the frequency of approximately once a month. If the residual life evaluation data of the apparatus/members are also supplied to the plant chart 11 and stored as plant chart data, this is effective in abnormality monitoring from the plant status variables described in the above embodiment. More specifically, the residual life evaluation data can be utilized as supplementary information to confirm abnormal signs estimated from other monitored information, and changes in trend of those data can also be utilized as plant abnormality monitoring information to improve reliability of the diagnosis result of the abnormality condition predicting/abnormality diagnosing system 67. Likewise, by taking the diagnosis result as well into the plant chart 11, reliability of the evaluation result of the residual life evaluating system 47 can be improved. Incidentally, the condition predicting/abnormality diagnosing system 67 comprises an abnormality detecting section 671, a cause identifying section 672, an incidental event predicting section 673, and a countermeasure guidance section 674.

With the embodiment of FIG. 13, as described above, since the chart data specific to the plant are also updated upon occasion, i.e., at the time of inspection, repair and replacement, and the material degradations are quantitated based on the updated data, the accuracy of evaluating remaining lives of the apparatus/members is improved, and changes in the remaining lives of the apparatus/members due to material deterioration can be early detected to prepare the countermeasure with a wide margin. Therefore, the plan can be safely and economically operated for a long term. Particularly, in a nuclear power plant which requires an extensive maintenance, a corresponding maintenance program can be prepared to be executed in the periodical inspection while avoiding shutdown of the plant other than scheduled, making it possible to assign workers and prepare parts, material and equipment necessary for repair/replacement with a wide margin, and hence to lighten the inspection work. Further, because of the remaining lives being predicted with high accuracy, when the predicted lives of apparatus/members are sufficiently longer than design lives thereof, the initial repair/replacement program can also be changed so as to prolong the period of use continuously.

Accordingly, it is possible to avoid the preventive maintenance which is neither necessary nor urgent, reduce the

period and cost required for periodical inspection of the plant, and to achieve a reduction in the frequency of periodical inspection and an extension of the interval thereof. While the life and reliability are generally increased when only a member such as a pipe is repaired or replaced, there is a possibility that when an apparatus is subject to repair, replacement and/or overhaul check, the occurrence of troubles called initial failures may be increased on the contrary since then. Also, because apparatus characteristics are changed, the data accumulated so far in the plant chart as characteristics specific to the apparatus are totally renewed, which lowers the accuracy of the apparatus diagnosis. From this viewpoint as well, therefore, it is desirable to avoid the preventive security operation which has been diagnosed as neither necessary nor urgent. In addition, by allocating costs and persons to other important security operation, reliability of the preventative maintenance can be further improved.

The result of the residual life evaluation by the residual life evaluating system can be displayed in various ways. By indicating the result on the screen of a display such as CRT, by way of example, it is possible not only to inform plant operators and so on, who are looking at the screen, of the occurrence of future possible trouble in the plant, but also to make them visually understand the urgency of taking any measure and the effect of the measure. More specifically, as shown in FIG. 14, the whole or part of the plant is indicated on a display screen 48 and, by selecting a location of which residual life is to be evaluated, the result of the residual life evaluation on the selected location is displayed. The result can be displayed, e.g., in the form of a graph showing crack progress behavior, or with pseudo-color indication of a residual life distribution in the selected location or surroundings thereof so that the residual life and the location to be dealt with can be visually recognized in a moment. Further, by displaying the kind of time of an applicable security measure, and simultaneously providing the result of the residual life evaluation after implementing the security measure upon selection of the operator, the effect of the countermeasure can also be confirmed.

In the embodiment of FIG. 14, a degradation is quantitated by a group of support programs 49 using the data in the plant chart 11, comprised of plant data 51 and material data 52, to thereby prepare degradation data 50. The plant data 51 include plant parameters (power, flow speed, radiation dose, etc.), operation, repair and periodical inspection records, material specifications, structures and so on. The material data 52 include characteristics of repaired and welded portions, characteristics of improved materials and so on. The group of support programs 49 evaluates such factors as residual stress, flow induced vibration, grain boundary segregation, radiation embrittlement, H and He behavior in irradiated material, and water chemistry in the reactor. The degradation data 50 and the data in the plant chart 11 are combined to make up a data base 53. The residual life evaluating system 47 comprises an input/output routine 54, a residual life evaluating routine 55, and a countermeasure evaluating routine 56.

The input/output routine 54 serves to select the location to be evaluated and to display the evaluation result. The residual life evaluating routine 55 includes, as an inner hierarchy, a crack incubation time evaluating routine 57, a crack propagation length evaluating routine 58, and critical crack length evaluating routine 59. The crack incubation time evaluating routine 57 evaluates the time until microscopic cracks coalesce together through repeated breakdown and repair of the surface oxide film to become a macroscopic

crack which steadily propagates. The crack length evaluating routine 58 evaluates a crack propagation length from the crack propagation rate, based on active dissolution, hydrogen embrittlement, fatigue, etc. On the other hand, the critical crack length evaluating routine 59 evaluates, from fracture toughness etc., a critical crack length leading to fracture based on the evaluation result of material deterioration during the period of use. Further, based on the above evaluation results, the countermeasure evaluating routine 56 evaluates the necessity of any security action, a proper candidate for a preventive maintenance 60 (hydrogen injection, surface improvement, or repair/welding) and the implementation time thereof, as well as the resultant effect. The evaluation result is indicated on the display screen 48. As shown at one exemplified screen 48a, the period till a time t_1 represents a crack incubation time, and a time t_2 at which the crack propagation length 58 intersects the critical crack length 59 corresponds to the life. Then, a time t_3 corresponds to the extended life after the preventive maintenance 60.

By displaying the evaluation result as described above, there can be obtained advantages of enabling operators to visually understand the necessity, urgency and effectiveness of a preventive maintenance, and to get a support for proper judgment. In addition, reliability of the residual life evaluation is improved since the material degradation is quantitated depending on the personality of the plant.

A description will now be made of a practical example of the material residual life evaluation. The residual life evaluation is performed in two stages concerned with the crack generation behavior (crack incubation time evaluation) and the crack propagation behavior (crack propagation length evaluation). The crack incubation time is generally longer than a period in which the crack propagation leads to fracture, and is most important in the material residual life evaluation. For the crack incubation time, the method of evaluating generation possibility of a stress corrosion crack (SCC) proposed by Yamauchi, et al. (38-th Fushoku-Boshoku Toronkai (Corrosion and Anticorrosion Meeting), October 1991) can be utilized. Specifically, the relationship among a crack incubation time t_i determined by an experiment under accelerated condition for each of degradations, a crack incubation time t_s determined under reference condition, and an acceleration factor F_i in material deterioration, i.e., $t_i = t_s \times F_i$ (where $n=1,2,3 \dots, n$).

When a plurality of degradations exist, a crack incubation time t can be expressed as Equation 1 below. Also, a material deterioration acceleration factor F can be expressed as Equation 2 below, i.e., the product of the acceleration factors F_i :

$$t = t_s \times F \quad (1)$$

$$n.L.H.4$$

$$F = \prod(F_i) \quad (2)$$

$$i = 1.L.H.8$$

A reference time for the crack incubation time is defined, for example, as the time until the crack length reaches 50 mm. If the material deterioration acceleration factor is standardized such that the crack incubation time t is one year at $F=1$, the material deterioration acceleration factor F itself can be regarded as the crack incubation time. The material deterioration acceleration factor is defined on an assumption that a material stays under constant conditions, so that changes in the plant operating conditions are taken in as follows in the actual plant.

It is assumed that plant operation starts with normal water chemistry and that F value of an apparatus to be evaluated is 10, i.e., a 50 mm crack is expected to appear in 10 years. It is also assumed that after 7 years, the operating conditions are changed to Hydrogen water chemistry by hydrogen injection and F is changed to $F=50$ under this environment. In this case, $7/10$ of $F=10$ has been consumed under the old environment after the elapse of 7 years, and the residual life under the new environment is expressed by $F=50 \times (3/10)=15$. Thus, it is predicted that a crack having a length of 50 mm will appear 15 years later. In this way, by utilizing the data in the plant chart and taking into account changes in the plant operating conditions in the integral form, the crack incubation time of each component apparatus of the plant.

From the viewpoint of ensuring safety of the plant, it is desirable to perform the residual life evaluation based on prediction of only the crack incubation time. Particularly in the nuclear power plant, the presence of a crack is not allowed. However, the above-described evaluation using the material deterioration acceleration factor is not free from a prediction error due to utilization of the acceleration experimental data. The longer the prediction period, the greater is an absolute value of the error. On the other hand, if a safety factor in consideration of the error is set to be too large, the above-described purpose of avoiding the preventive maintenance which is neither necessary nor urgent cannot be sufficiently achieved. Furthermore, when the abnormality diagnosing system of the present invention has not yet been installed at start-up of the plant operation and is introduced after the plant operation, the crack propagation may have been already actualized.

Accordingly, predicting all of the crack generations until actualization of microscopic cracks is thought to be practically difficult, and hence evaluation of the crack propagation behavior is also important in the residual life evaluation. In this case, a crack whose length is larger than a detection limit is detected during inspection and check. The detection limit of the crack length is approximately 1 mm. An important point in the residual life evaluation when a crack is detected is the crack propagation rate. How the crack propagation rate will change in future is evaluated using the data in the plant chart.

For a stress corrosion cracking (SCC), several models adapted for, e.g., an active dissolution at the crack tip are proposed, and the data required for evaluation, such as a strain rate at the crack tip, are taken out of the plant chart. In the case where the plant chart data before introduction of the abnormality diagnosing system are not present, the record until the present time is estimated as with the future estimation, and the crack propagation rate is evaluated based on the estimated record. While the above description is made in connection with the SCC in a nuclear power plant, SCC's in other plants and other deterioration mechanisms such as fatigue cracking can also be handled in a like manner.

In the above-described embodiment, the crack propagation behavior in the reactor internals of the nuclear power plant is evaluated by separating the behavior into two states of generation and propagation. However, the evaluation may be performed by further dividing each of the generation and the propagation into, e.g., generation and coalescence of microscopic cracks, or by correlating them depending upon the evaluation accuracy of a residual life and the material deteriorating mechanism. This is similarly applied to the material degradations described above in connection with FIG. 14. In other words, the material degradations are omitted, selected and added as need.

In selecting the location to be evaluated and the countermeasure, by carrying on a dialogue through a

display, the evaluation can be performed while visually confirming all of the procedures. When the location to be evaluated is selected in a plant structure image on the display screen using a pen, a mouse or the like, the items to be confirmed, such as the apparatus/member name and the material name, are displayed. Upon confirming the items, as shown in FIG. 15, an enlarged image of the selected location and its vicinity is displayed in an increasing enlarged scale, e.g., in order of 48A to 48B to 48C. By so repeating the step of confirming the times such as the apparatus/member name and the material name, the objective apparatus/member is finally selected. By gradually enlarging the location to be evaluated, it is possible to clarify which portion of the objective apparatus/member is subject to problematic deterioration and how the situation is improved by which countermeasure. Of course, by displaying and reviewing an entire image of the plant, soundness of the whole plant can be grasped.

The place where the residual life evaluating system is installed is not limited to a central control room of the plant.

Generally, with a possibility of material deterioration progressing quickly being small as opposed to an apparatus abnormality, if the plant periodical inspection is surely performed, the evaluation result is often only required to be available in determining a relatively long-term action such as a maintenance program till the next periodical inspection or the periodical inspection after the next. The information resulted in such a case is not to be handled by plant operators. Therefore, the residual life evaluating system may be installed in an other plant facility, e.g., a preventive maintenance center, so that a maintenance program including, e.g., how to ensure apparatus and materials used in repair/replacement of the apparatus/members to be dealt with by the maintenance program, equipment required for engineering, and person can be determined in coordination with maintenance programs for other plants. This enables the long-term plant security to be achieved while making best use of resources including manpower.

While the above embodiments are described as applying the present invention to a nuclear power plant, the invention is also applicable to other facilities, such as various types of thermoelectric power plants and chemical plants for producing ethylene, in addition to the nuclear power plant.

The present invention arranged as described hereinabove has the following advantages.

In the plant monitoring and diagnosing method, a plant operating condition, an apparatus operating condition and an environment condition are detected, detection data are accumulated, plant inspection data are accumulated, and the plant condition is diagnosed based on plant record information consisted of the accumulated detection data and inspection data. Therefore, it is possible to realize the plant monitoring and diagnosing method which can exactly analyze and diagnose an abnormality with high reliability, taking into account the production record, the check/repair record and the operation record of a plant, and can simplify the periodical inspection, resulting in a higher availability factor of the plant.

Also, in the plant monitoring and diagnosing system, the system comprises a first input section for receiving detection data of a plant operating condition, an apparatus operating condition and an environment condition, a second input section for receiving plant inspection data, a first input data processing section for preparing data for use in plant monitoring and diagnosis based on the detection data from the first input section, a second input data processing section for preparing data for use in plant monitoring and diagnosis

based on the inspection data from the second input section, a plant chart for storing the data prepared by the first and second input data processing sections, and a monitoring and diagnosing section for monitoring and diagnosing the plant condition based on the data stored in the plant chart. Therefore, it is possible to realize the plant monitoring and diagnosing system which can exactly analyze and diagnose and abnormality with high reliability, taking into account the production record, the check/repair record and the operation record of a plant, and can simplify the periodical inspection, resulting in a higher availability factor of the plant.

What is claimed is:

1. A method of monitoring and diagnosing plant conditions comprising:

a first step of inputting a first set of detection data of a first type relating to a given characteristic of a plant element to be diagnosed; inputting a second set of detection data of a second type relating to said given characteristic but different from said first type of detection data; determining a correlation between said first set of detection data; calibrating said determined correlation using said second set of detection data; and storing said calibrated correlation as a plant chart for monitoring and diagnosis; and

a second step of comparing said calibrated correlation stored as a plant chart and a correlation of a third set of detection data, said third set of detection data being of said first type, to monitor and diagnose an abnormality in the plant element.

2. A method of monitoring and diagnosing plant conditions according to claim 1, wherein when an abnormality is diagnosed in said second step, an abnormal location and abnormal details are identified and an event which will ensue from the abnormality is predicted.

3. A method of monitoring and diagnosing plant conditions according to claim 2, wherein said identified abnormal location and details and said event which will ensue from the abnormality are indicated by display means.

4. A method of monitoring and diagnosing plant conditions according to claim 2, wherein a countermeasure for dealing with the detected abnormality is selected, and said identified abnormal location and details, said event which will ensue from the abnormality, and a countermeasure are indicated by display means.

5. A method of monitoring and diagnosing plant conditions comprising:

a first step of inputting a plurality of different detection data relating a given plant operating condition; determining a first plurality of values defining said plurality of different detection data; and storing a first correlation of said first plurality of values as a plant chart for monitoring and diagnosis; and

a second step of comparing said first correlation of said first plurality of values stored as a plant chart and a correlation of a second plurality of values, said second plurality of values being current values defining said plurality of different detection data to monitor and diagnose an abnormality in a plant element relating to said plant operating condition;

wherein when an abnormality is diagnosed in the second step, a location of the abnormality and a plurality of details regarding an event which will ensue from the abnormality are predicted and indicated on a display means, and wherein a countermeasure for responding

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to the details regarding the ensuing event is also predicted and indicated on a display means.

6. A method of monitoring and diagnosing plant conditions according to claim 1 or 2, wherein said first step further includes a step of inputting inspection data from a plant; and taking said inspection data into consideration to determine said correlation as a plant chart for monitoring and diagnosis.

7. A method of monitoring and diagnosing plant conditions according to claim 5, wherein a residual life for said plant element is evaluated based on the data in the plant chart and material degradation data calculated from the plant chart data.

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8. A method of monitoring and diagnosing plant conditions according to claim 7, wherein said first step further comprises inputting inspection data from a plant; and

an effect of crack propagation is evaluated based on the data in the plant chart, the inspection data, and the material degradation data, in terms of a crack incubation time until microscopic cracks coalesce to become a macroscopic crack, a propagation length of the macroscopic crack, and a critical crack length which reflects deterioration of the material strength, thereby evaluating a residual life for said plant element.

* * * * *



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(45) **Date of Patent:** ***Jul. 10, 2001**

(54) **CATALYTIC HYDROGEN PEROXIDE
DECOMPOSER IN WATER-COOLED
REACTORS**

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(List continued on next page.)

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(*) **Notice:** This patent issued on a continued pro-
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1.53(d), and is subject to the twenty year
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376/417**

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376/414, 417, 900**

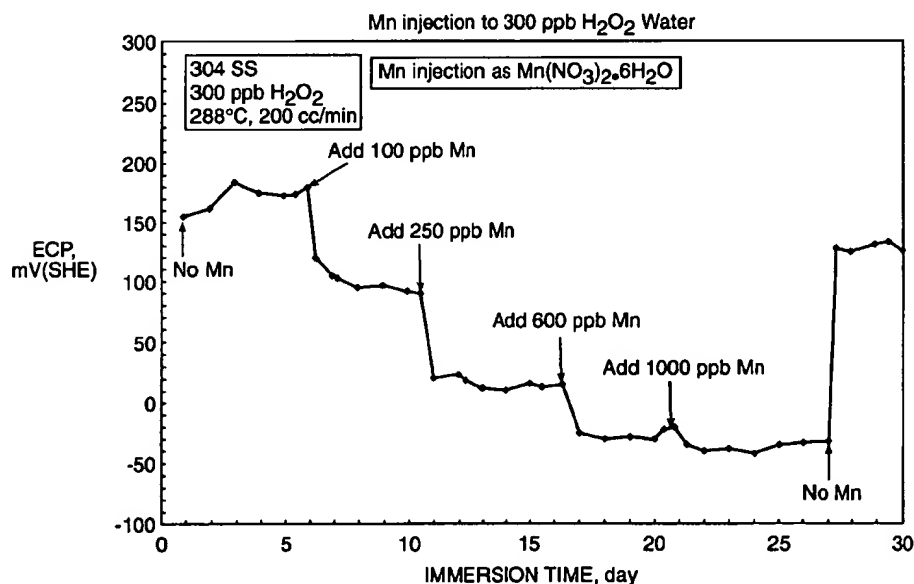
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(57) ABSTRACT

A metal cooling tube of a water-cooled nuclear reactor, having an inner surface thereof exposed to an aqueous cooling medium containing hydrogen peroxide. The cooling tube has its inner surface coated with matter selected from the group consisting of the element manganese, molybdenum, zinc, copper, cadmium for absorbing such hydrogen peroxide and then affecting decomposition of the hydrogen peroxide in the aqueous medium. In preferred embodiment such coating is manganese and oxides thereof. A method for lowering the electrochemical corrosion potential of a metal alloy cooling tube exposed to an aqueous medium in a water-cooled nuclear reactor is also disclosed. Such method comprises the step of coating an inner surface of such tube with matter selected from the group of elements comprising manganese, molybdenum, zinc, copper, cadmium, so as to permit absorption and hydrogen peroxide in such aqueous medium and effect decomposition of hydrogen peroxide in such aqueous medium.

12 Claims, 5 Drawing Sheets

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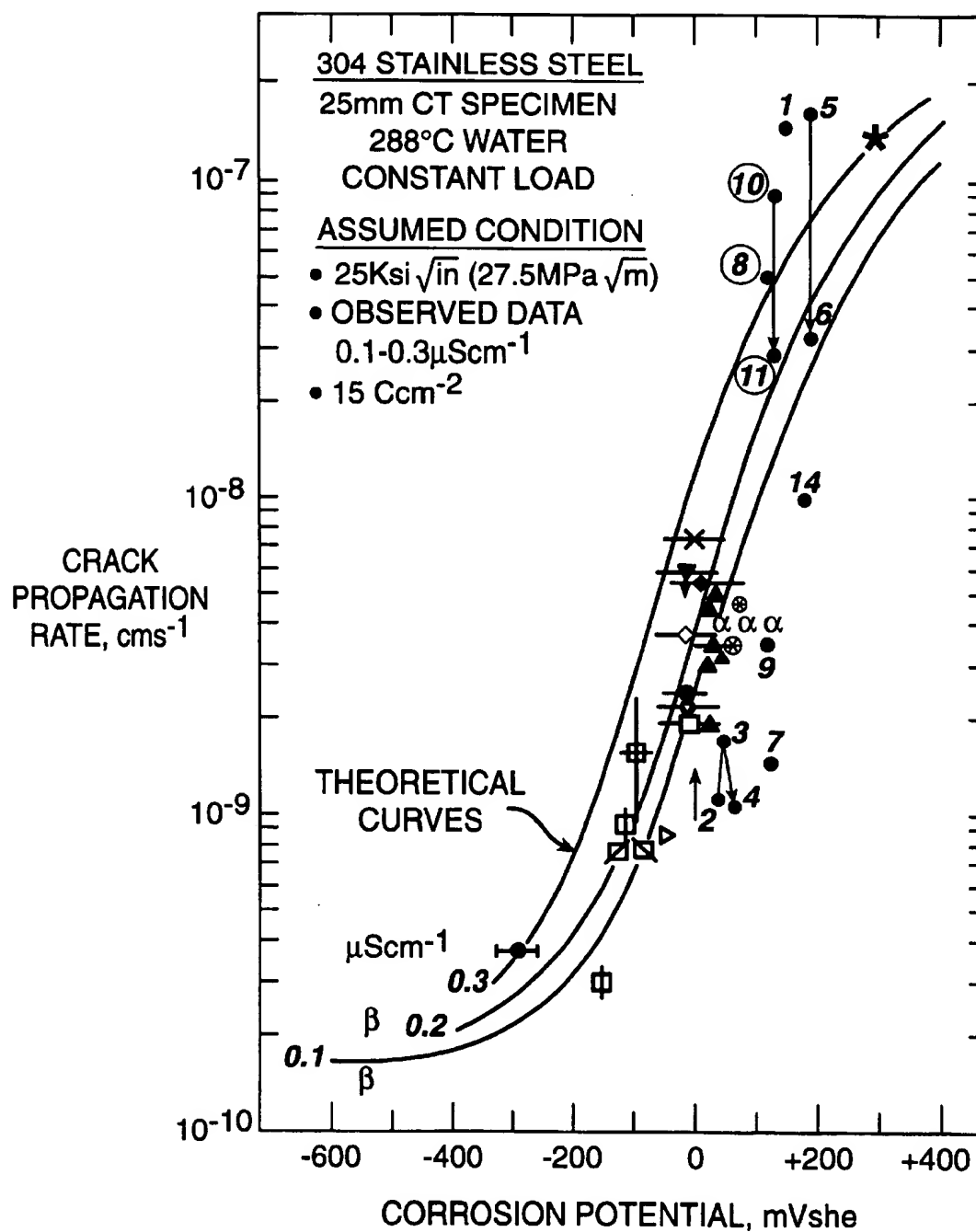
FIG. 1

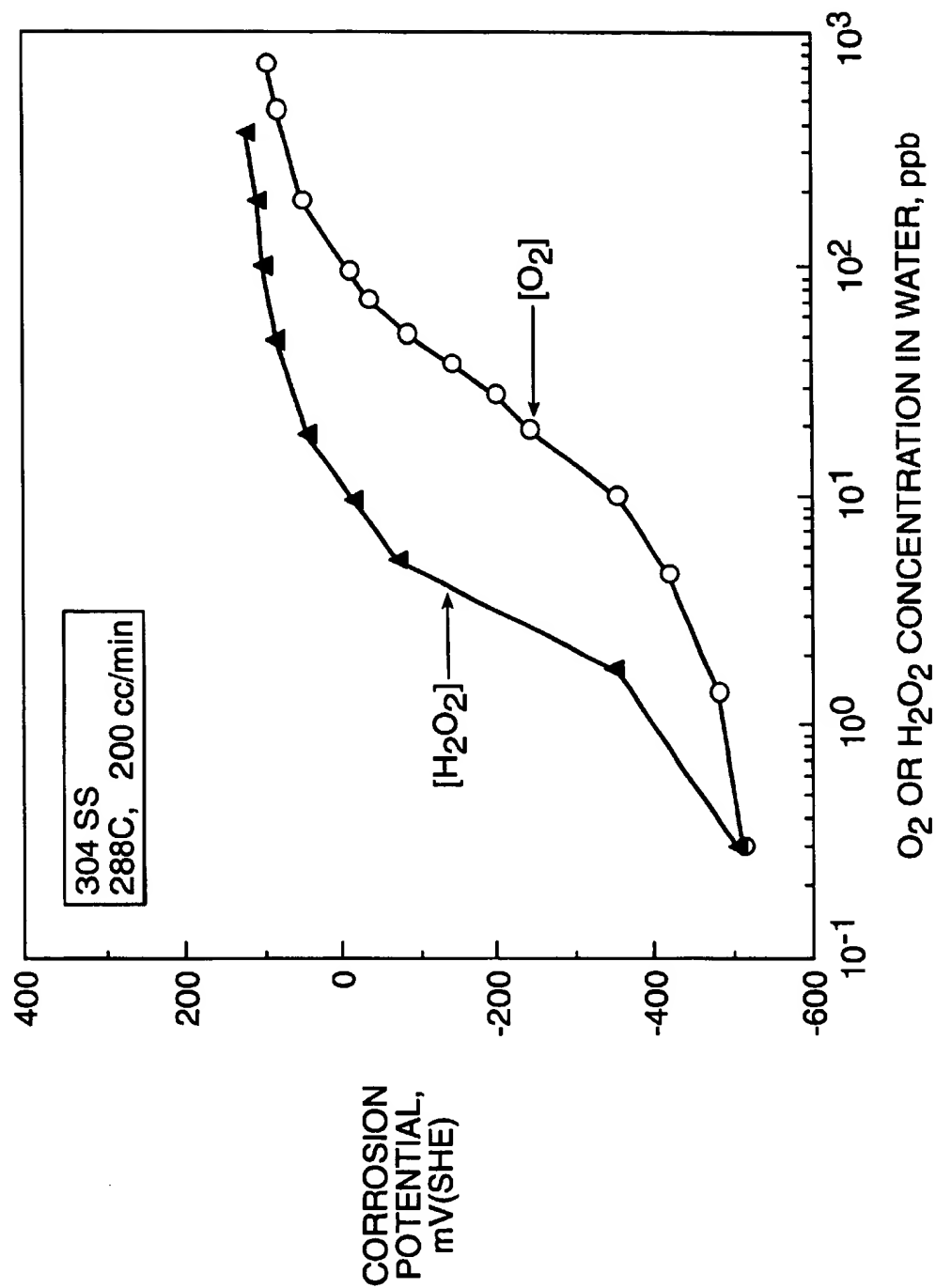
FIG. 2

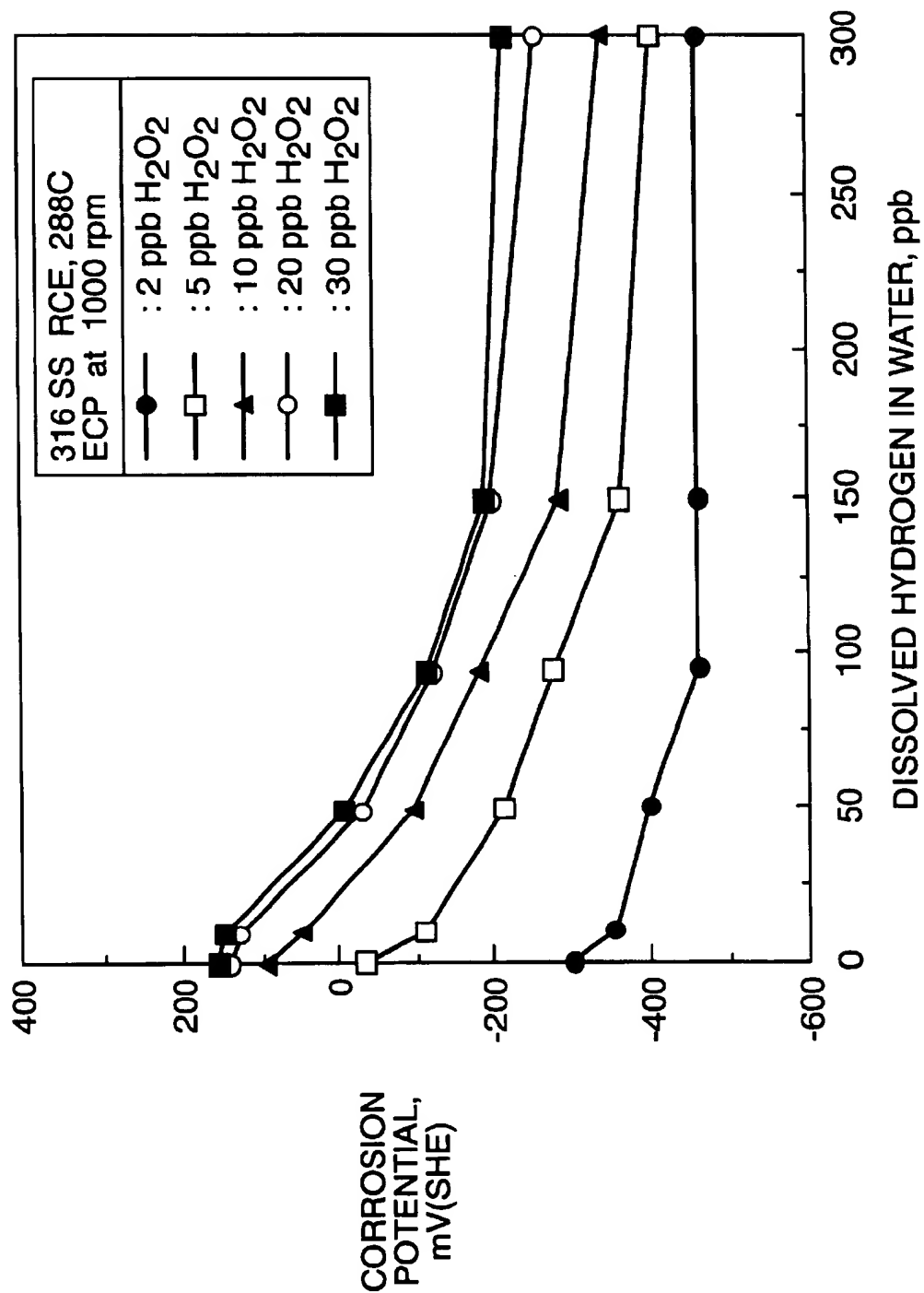
FIG. 3

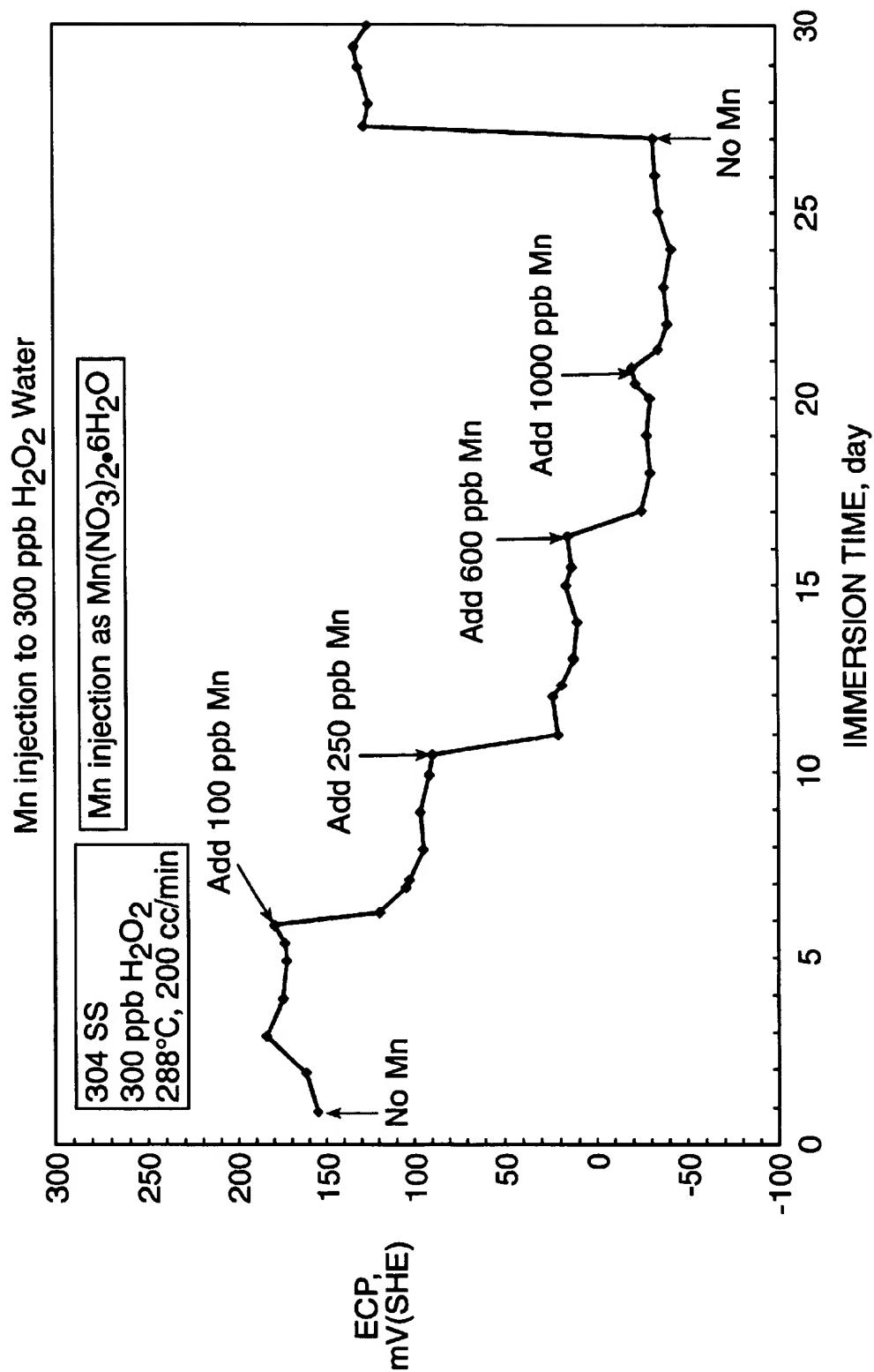
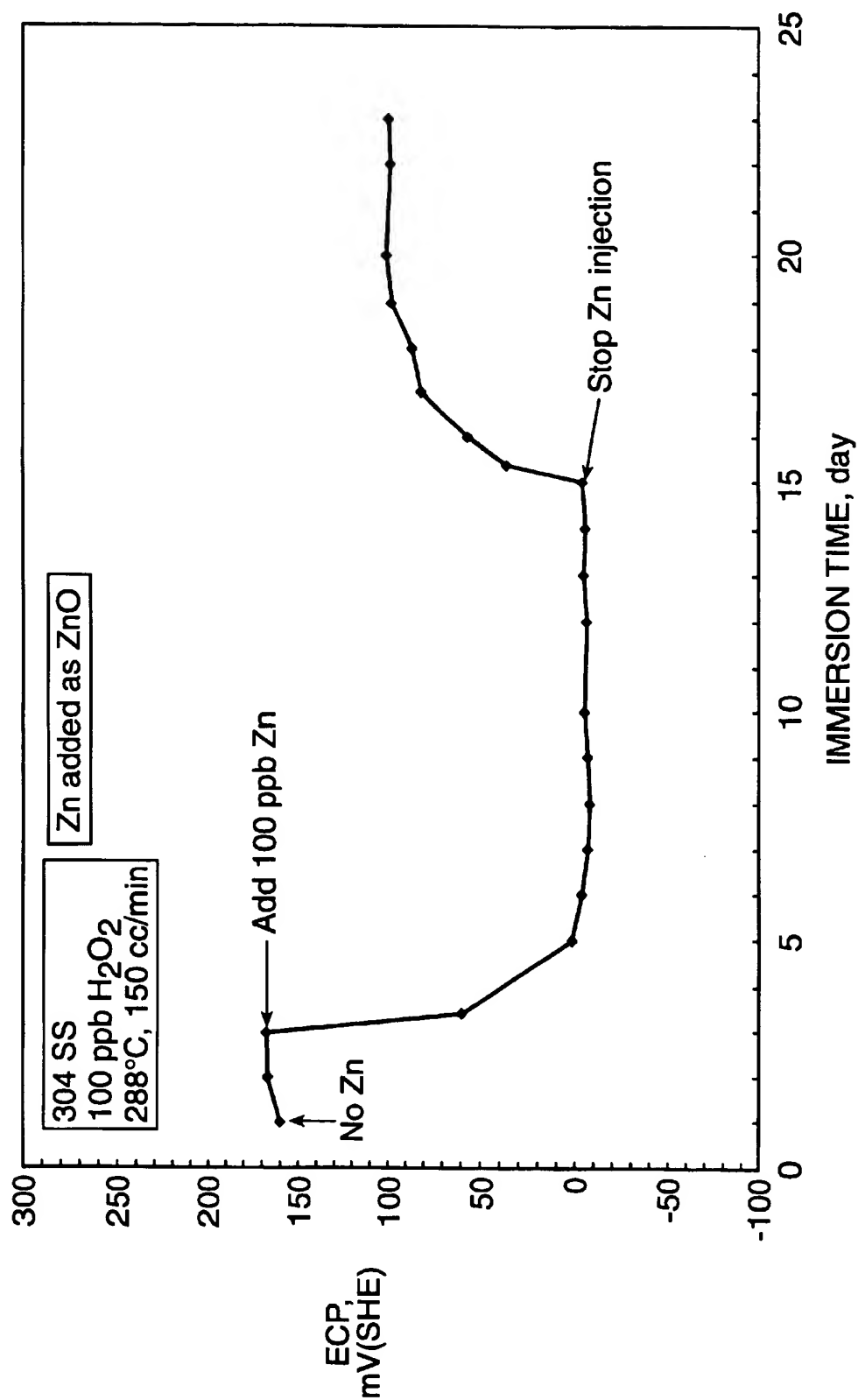
FIG. 4

FIG. 5

CATALYTIC HYDROGEN PEROXIDE DECOMPOSER IN WATER-COOLED REACTORS

BACKGROUND OF THE INVENTION

The present invention is directed to hydrogen peroxide decomposer for use in water-cooled nuclear reactors, including boiling water reactors and pressurized water reactors, for the mitigation of corrosion phenomena in such systems.

Steel pressure vessels and piping exposed to high temperature water are prone to corrosion due to oxidation of the various metals therein by oxidizing agents, particularly oxygen, present in the high temperature water. Corrosion of such vessels and piping can lead to a variety of problems, including stress corrosion cracking, crevice corrosion and erosion corrosion, leading to leakage and/or bursting of such vessels and piping.

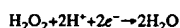
In nuclear reactors, significant amounts of heat energy is generated by reactor processes occurring in the reactor core. A liquid coolant, typically water, is used to remove heat from the reactor core and facilitate its conversion to a useable form. A reactor vessel is provided to contain the reactor coolant around the reactor core to effect such heat removal. Further, piping is provided to facilitate transport of the coolant to steam generators or turbines, where heat energy is ultimately converted to electricity. The materials used in the construction of nuclear reactor vessels and piping are elected for their ability to withstand rigorous loading, environmental and radiation conditions. Such materials include carbon steel, low alloy steel, stainless steel and nickel-based, cobalt-based and zirconium-based alloys.

Despite careful material selection, corrosion and, particularly, intergranular stress corrosion cracking (or, simply, stress corrosion cracking (SCC)), is a problem in steel pressure vessels and piping used in nuclear reactors. SCC, as used herein, refers to cracking propagated by static or dynamic tensile stressing in combination with corrosion at the crack tip. Unfortunately, the nuclear reactor environment is conducive to both tensile stressing and corrosion.

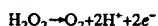
Nuclear reactor pressure vessels and piping are subject to a variety of stresses. Some are attributable to the high operating pressure required to maintain high temperature water in a liquid state. Stresses also arise due to differences in thermal expansion of the materials of construction. Other sources include residual stresses from welding, cold working, and other metal treatments.

Nuclear reactors are also susceptible to SCC because of the water chemistry environment of its process systems, which is favourably disposed to corrosion. In this respect, the presence of oxidizing agents, such as oxygen, hydrogen peroxide, and various short-lived radicals, which arise from the radiolytic decomposition of high temperature water in boiling water reactors, contribute to SCC.

Hydrogen peroxide is particularly unstable as it has the ability to act as both an oxidizing agent and a reducing agent. Hydrogen peroxide can act as an oxidizing agent, leading to the formation of water according to the following reaction:

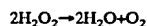


As a reducing agent, hydrogen peroxide is oxidized to oxygen according to the following reaction:



Because of its ability to act as both an oxidizing agent and a reducing agent, hydrogen peroxide is highly unstable and

will spontaneously decompose into water and oxygen according to the following reaction:



This will happen if aqueous hydrogen peroxide contacts a metallic surface whose electrode potential lies within this region of instability, which is typically the case in the BWR environment.

Stress corrosion cracking is of great concern in boiling water reactors (BWR's) which utilize light water as a means of cooling nuclear reactor cores and extracting heat energy produced by such reactor cores. Stress corrosion cracking causes leakage or bursting of such vessels or piping resulting in the loss of coolant in the reactor core. This compromises the reactor process control, which could have dire consequences.

To mitigate stress corrosion cracking phenomenon in BWR's, it is desirable to reduce the electrochemical corrosion of metal components that are exposed to aqueous fluids. ECP Electrochemical Corrosion Potential is a measure of the thermodynamic tendency for corrosion to occur, and is a fundamental parameter in determining rates of stress corrosion cracking. ECP has been clearly shown to be a primary variable in controlling the susceptibility of metal components to stress corrosion cracking in BWRs. FIG. 1 shows the observed and predicted crack growth rate as a function of ECP for furnace sensitized Type 304 stainless steel at 27.5 MPa in 288° C. water over the range of solution conductivities from 0.1 to 0.3 $\mu\text{S}/\text{cm}$.

For type 304 stainless steel (containing 18–20% Cr, 8–10.5% Ni, and 2% Mn), it is known that if the ECP of such steel exposed to high temperature water at about 288° C. can be reduced to values below –230 mV (Standard Hydrogen Electrode—SHE) (hereinafter the “critical corrosion potential”), the stress corrosion cracking problem of such steel can be greatly reduced. The same generally applies for other types of steels.

A well-known method to reduce the ECP to less than –230 mV_{SHE} and thereby mitigate SCC of steel pressure vessels and piping in nuclear reactors, is to inject hydrogen gas to the recirculating reactor feedwater. The injected hydrogen gas reduces oxidizing species in the water, such as dissolved oxygen. This has the very desirable benefit of reducing the corrosion potential of the steel vessel or piping carrying such high temperature water.

As illustrated in FIG. 2, ECP of 304SS in 288° C. water increases more rapidly with continued addition of hydrogen peroxide when compared to the ECP values measured at the same levels of oxygen concentration. Further, even with the use of hydrogen gas injection, SCC in BWRs continues to occur at unacceptable rates when hydrogen peroxide is present. This is illustrated in FIG. 3, where stress corrosion cracking is shown to occur in BWRs, even with the addition of hydrogen gas, when 20–30 ppb of hydrogen peroxide is present. This information suggests that the presence of hydrogen peroxide in reactor systems is a significant contributor to stress corrosion cracking of metal components. Moreover, the present practice of injecting hydrogen gas into the process liquid does not appear to completely assist in the decomposition of hydrogen peroxide and therefore does not bring about the concomitant reduction in ECP that is expected.

SUMMARY OF INVENTION

In one broad aspect, the present invention provides a corrosion resistant alloy having a surface exposed to aque-

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ous liquid consisting of oxidizing species, including hydrogen peroxide, that increase the ECP of the alloy. The surface of the alloy is coated with a coating comprised of Mn, Mo, Zn, Cu, Cd, oxides thereof, or chemical compounds thereof. These metals and their compounds assist in causing the decomposition of hydrogen peroxide, thereby reducing the ECP of the alloy. These metals and their compounds can be present as a pre-existing coating on the alloy, or may be deposited in-situ into the aqueous liquid for subsequent deposition on the surface of the alloy after injection.

According to another broad aspect of the present invention there is provided a corrosion resistant alloy cooling tube in a water-cooled nuclear reactor having a surface exposed to an aqueous cooling medium containing hydrogen peroxide, the surface being coated with a coating comprising matter selected from the group consisting of manganese, molybdenum, zinc, copper, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, for causing decomposition of the hydrogen peroxide.

According to another aspect of the present invention there is provided a water-cooled nuclear reactor comprising metal piping, such metal piping having a surface exposed to an aqueous liquid containing hydrogen peroxide, the surface being coated with a coating comprising matter selected from the group consisting of manganese, molybdenum, zinc, copper, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, for causing decomposition of the hydrogen peroxide.

According to another aspect of the present invention there is provided a method for lowering the electrochemical corrosion potential of a metal alloy, for use in a cooling tube in a water-cooled nuclear reactor, having a surface exposed to an aqueous liquid containing hydrogen peroxide, comprising the step of coating the surface with matter selected from the group consisting of manganese, molybdenum, zinc, copper, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, for causing decomposition of the hydrogen peroxide.

In a further aspect of the present invention, there is provided a method of lowering the electrochemical corrosion potential of metal alloy cooling tubes in a water-cooled nuclear reactor, the tubes having surfaces exposed to an aqueous liquid containing hydrogen peroxide, comprising the step of injecting matter into said water, said matter selected from the group consisting of manganese, molybdenum, zinc, copper, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, for causing decomposition of the hydrogen peroxide.

BRIEF DESCRIPTION OF THE DRAWINGS

The method and apparatus of the invention will now be described with reference to the accompanying drawings, in which:

FIG. 1 is a graph illustrating the observed and theoretical crack propagation rate as a function of electrochemical corrosion potential for sensitized 304 stainless steel in 288° C. water under constant load (25 ksi/in);

FIG. 2 is a graph illustrating electrochemical corrosion potential for 304 stainless steel in 288° C. water containing various amounts of H₂O₂ showing corrosion potential of such 304 stainless steel as a function of the O₂ and H₂O₂ concentration in water.

FIG. 3 is a graph illustrating the electrochemical corrosion potential for 316 stainless steel in 288° C. water containing various amounts of H₂O₂ showing corrosion potential of such 316 stainless steel in as a function of

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dissolved H₂ concentration in water with varying amounts of hydrogen peroxide.

FIG. 4 is a graph illustrating the electrochemical corrosion potential of 304 stainless steel in 288° C. water containing 300 parts per billion hydrogen peroxide with and without in-situ injection of various manganese concentrations as a function of immersion time.

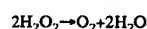
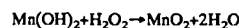
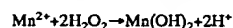
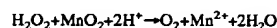
FIG. 5 is a graph illustrating the electrochemical corrosion potential of 304 stainless steel in 288° C. water containing 100 parts per billion hydrogen peroxide with and without in-situ injection of various zinc concentrations as a function of time.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that, by coating an alloy from the group consisting of carbon steel, alloy steel, stainless steel, nickel-based alloys, zirconium and cobalt-based alloys with a catalytically active material, or otherwise providing catalytic activity at such metal alloy surfaces, the decomposition of the hydrogen peroxide in aqueous process systems of nuclear reactors is catalysed by the catalytically active material. Such catalytic action at the surface of the alloy reduces the ECP of the alloy, thereby mitigating SCC of such alloy. Suitable coatings of catalytically active material can be deposited by methods well known in the art for depositing continuous or substantially continuous coatings on metal substrates, such as plasma spraying, chemical vapour deposition, physical vapour deposition processes such as sputtering, welding such as metal inert gas welding, electroless plating, and electrolytic plating.

The catalytically active material can be a metal selected from the group consisting of manganese, molybdenum, zinc, copper, cadmium and mixtures thereof. Other suitable materials include oxides of these metals. Even further suitable materials can include chemical compounds containing these metals, where the metal in such compounds is able to dissociate and make itself available for reacting with oxygen to form an oxide.

Manganese dioxide catalyzes the decomposition of hydrogen peroxide according to the following reaction mechanism:



It is believed that, by coating the surface of a metal alloy cooling tube of a water-cooled nuclear reactor with manganese, such component is able to maintain a lower ECP. This is because the manganese is believed to be oxidized to catalytically active manganese oxide (MnO₂), which catalyses hydrogen peroxide decomposition.

Because very small surface concentrations are adequate to provide the necessary catalytic activity and reduce the corrosion potential of the metal, the processing as well as the physical, metallurgical or mechanical properties of the alloys and components formed therefrom are not significantly altered. Further, lower amounts of reducing species, such as hydrogen, are necessary to reduce the ECP of the metal components below the critical potential, because of the catalysed decomposition of hydrogen peroxide.

As an alternative to coating the subject alloy with the catalytically active material, the catalytically active material

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may be injected in-situ in the process liquid for effecting decomposition of hydrogen peroxide, thereby reducing the ECP of the alloy. FIG. 4 shows the benefits of in-situ injection of manganese as $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for effecting decomposition of hydrogen peroxide. With each injection, there was a corresponding reduction in ECP of the alloy believed attributable to the decomposition of hydrogen peroxide. It is believed that the injected manganese oxidizes and precipitates out as MnO_2 on the alloy surface. Once deposited on the surface, MnO_2 effects the catalytic decomposition of hydrogen peroxide according to the above-described reaction mechanism.

The present invention will be described in further detail with reference to the following non-limitative examples.

EXAMPLE 1

A 304 SS electrode was placed in an autoclave recirculating loop, containing water at 288°C . having 300 ppb hydrogen peroxide. Various concentration of dissolved Mn solution were injected directly into the autoclave where the 304 SS electrode was immersed and argon gas was continuously purged through this injection solution during the test. The ECP of the 304 SS electrode was measured over the course of 30 days using a $\text{Cu}/\text{Cu}_2\text{O}/\text{ZrO}_2$ electrode. The measured ECP was converted to a standard hydrogen electrode (SHE) scale.

FIG. 4 shows the ECP response of 304 SS electrode before, during, and after three different manganese solution injections to 288°C . water containing 300 ppb hydrogen peroxide. It is evident that the addition of Mn to 300 ppb hydrogen peroxide water decreased the ECP of the 304 SS electrode. Once injections were ceased, the ECP of the 304 SS electrode remained lower than the corrosion potential observed before the injections were commenced. This indicates the possible deposition of manganese oxide on 304 SS oxide, with the concomitant catalytic decomposition of hydrogen peroxide by the deposited manganese. The presence of manganese was, in fact, confirmed by Auger electron spectroscopy, which confirmed a thin oxide layer of 2-4% by weight on the 304 SS surface, to a depth of 100-150 Å.

From the above test, the presence of manganese oxide on the metal surfaces enhances the decomposition of hydrogen peroxide, with a consequent decrease in ECP of the metal alloy.

EXAMPLE 2

A 304 SS electrode was placed in an autoclave recirculating loop, containing water at 288°C . having 100 ppb hydrogen peroxide. Zinc, as zinc oxide, was injected directly into the autoclave where the 304 SS electrode was immersed. The ECP of the 304 SS electrode was measured over the course of 25 days using a $\text{Cu}/\text{Cu}_2\text{O}/\text{ZnO}_2$ electrode. The measured ECP was converted to a standard hydrogen electrode (SHE) scale.

FIG. 5 shows the ECP response of 304 SS electrode before, during and after aqueous zinc oxide injection to 288°C . water containing 100 ppb hydrogen peroxide. Clearly, once injection of the aqueous Zinc oxide began, ECP of the 304 SS became reduced. Once injection was stopped, the ECP of the 304 SS electrode remained lower than the corrosion potential observed before the injections were commenced. This indicates the possible deposition of zinc oxide on 304 SS, with the concomitant decomposition of hydrogen peroxide by the deposited zinc oxide.

The present invention provides a number of important advantages. In particular, the present invention provides a

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metal alloy surface coated with a catalytically active material for the decomposition of hydrogen peroxide. By doing so, the ECP of such metal alloys is lowered, thereby reducing corrosion and, notably, mitigating the effects of stress corrosion cracking. This is particularly beneficially for components of water-cooled nuclear reactors, whose high temperature aqueous environment is conducive to such corrosion phenomena, and where the occurrences of such phenomena could lead to loss of coolant and consequent loss of reactor control.

It will be understood, of course, that modifications can be made in the embodiments of the invention described herein without departing from the scope and purview of the invention. For a complete definition as to the scope of the invention, reference is to be made to the appended claims.

We claim:

1. A structure material for a cooling tube of a water-cooled nuclear reactor having a surface exposed to an aqueous cooling medium containing hydrogen peroxide, said surface coated with a coating comprising matter selected from the group consisting of manganese, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, the structure material being sufficient for effecting and causing decomposition of said hydrogen peroxide in said cooling medium.

2. The structure material as claimed in claim 1 wherein said alloy is selected from the group consisting of carbon steel, zirconium, alloy steel, stainless steel, nickel-based alloys, and cobalt-based alloys.

3. The structure material as claimed in claim 1 wherein said matter of said coating is capable of adsorbing said hydrogen peroxide.

4. The structure material as claimed in claim 3 wherein the coating is deposited by a process selected from the group consisting of plasma spraying, chemical vapour deposition, physical vapour deposition, welding, electroless plating and electrolytic plating.

5. A structure material for a water-cooled nuclear reactor comprising metal piping, said metal piping having a surface exposed to an aqueous liquid containing hydrogen peroxide, the structure material comprising a coating, the coating comprising matter selected from the group consisting of manganese, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, said coating being sufficient for effecting and causing decomposition of said hydrogen peroxide in said aqueous liquid.

6. The structure material for a nuclear reactor as claimed in claim 5 wherein said metal piping is comprised of alloys selected from the group consisting of carbon steel, alloy steel, zirconium, stainless steel, nickel-based alloys, cobalt-based alloys and mixtures thereof.

7. The reactor as claimed in claim 6 wherein said matter of said coating is capable of adsorbing said hydrogen peroxide.

8. The reactor as claimed in claim 7 wherein said piping surface coating is deposited by a process selected from the group consisting of plasma spraying, chemical vapour deposition, physical vapour deposition, welding, electroless plating and electrolytic plating.

9. A method for lowering the electrochemical corrosion potential of a metal alloy for use in a cooling tube in a water-cooled nuclear reactor having a surface exposed to an aqueous liquid containing hydrogen peroxide, comprising the step of coating said surface with matter selected from the group consisting manganese, copper, cadmium, oxides thereof, chemical compounds thereof and mixtures thereof, said coating being sufficient for effecting and causing decomposition of said hydrogen peroxide.

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10. The method as claimed in claim 9 wherein said metal alloy is selected from the group consisting of carbon steel, alloy steel, stainless steel, zirconium nickel-based alloys, and cobalt-based alloys and mixtures thereof.

11. The method as claimed in claim 10 wherein said matter is capable of adsorbing said hydrogen peroxide in said liquid.

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12. The method as claimed in claim 11 wherein said matter is deposited by a process selected from the group consisting of plasma spraying, chemical vapour deposition, physical vapour deposition, welding, electroless plating, electrolytic plating and mixtures thereof.

* * * * *



US005768330A

United States Patent [19]

Andresen et al.

[11] **Patent Number:** 5,768,330[45] **Date of Patent:** *Jun. 16, 1998

[54] **CO-DEPOSITION OF PALLADIUM DURING OXIDE FILM GROWTH IN HIGH-TEMPERATURE WATER TO MITIGATE STRESS CORROSION CRACKING**

[75] **Inventors:** Peter Louis Andresen, Schenectady, N.Y.; Samson Hettiarachchi, Menlo Park, Calif.; Young Jin Kim, Clifton Park, N.Y.; Thomas Pompilio Diaz, San Martin, Calif.

[73] **Assignee:** General Electric Company, Schenectady, N.Y.

[*] **Notice:** The term of this patent shall not extend beyond the expiration date of Pat. No. 5,581,588.

[21] **Appl. No.:** 729,024

[22] **Filed:** Oct. 10, 1996

Related U.S. Application Data

[60] Division of Ser. No. 322,253, Oct. 13, 1994, Pat. No. 5,608,766, which is a continuation-in-part of Ser. No. 265,598, Jun. 24, 1994, abandoned, Ser. No. 209,175, Mar. 10, 1994, abandoned, Ser. No. 143,513, Oct. 29, 1993, abandoned, and Ser. No. 143,514, Oct. 29, 1993, Pat. No. 5,448,605.

[51] **Int. Cl.⁶** G21C 9/00

[52] **U.S. Cl.** 376/305; 376/301; 376/306; 422/11; 422/14; 422/19

[58] **Field of Search** 376/301, 305, 376/306, 356, 357; 422/11, 14, 19

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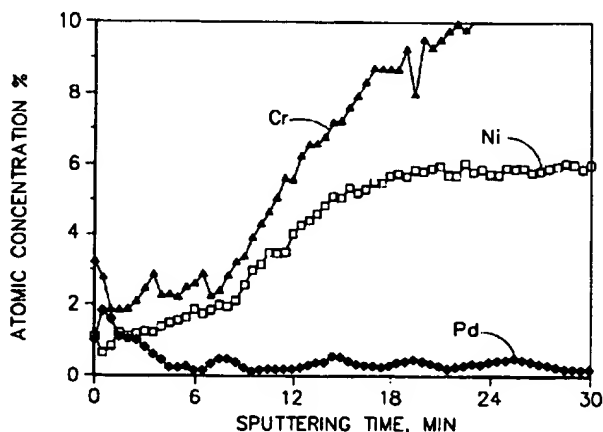
Primary Examiner—Kathryn L. Gorgos

Assistant Examiner—Chrisman D. Carroll

Attorney, Agent, or Firm—Nixon & Vanderhye

[57] **ABSTRACT**

A method for improving the performance and longevity of coatings of metal deposited from aqueous solutions of inorganic, organic or organometallic metal compounds. The method involves co-deposition of noble metal or corrosion-inhibiting non-noble metal during growth of oxide film on a component made of alloy, e.g., stainless steels and nickel-based alloys. The result is a metal-doped oxide film having a relatively longer life in the reactor operating environment. In particular, incorporation of palladium into the film provides greatly increased catalytic life as compared to palladium coatings which lie on the oxide surface.

2 Claims, 5 Drawing Sheets

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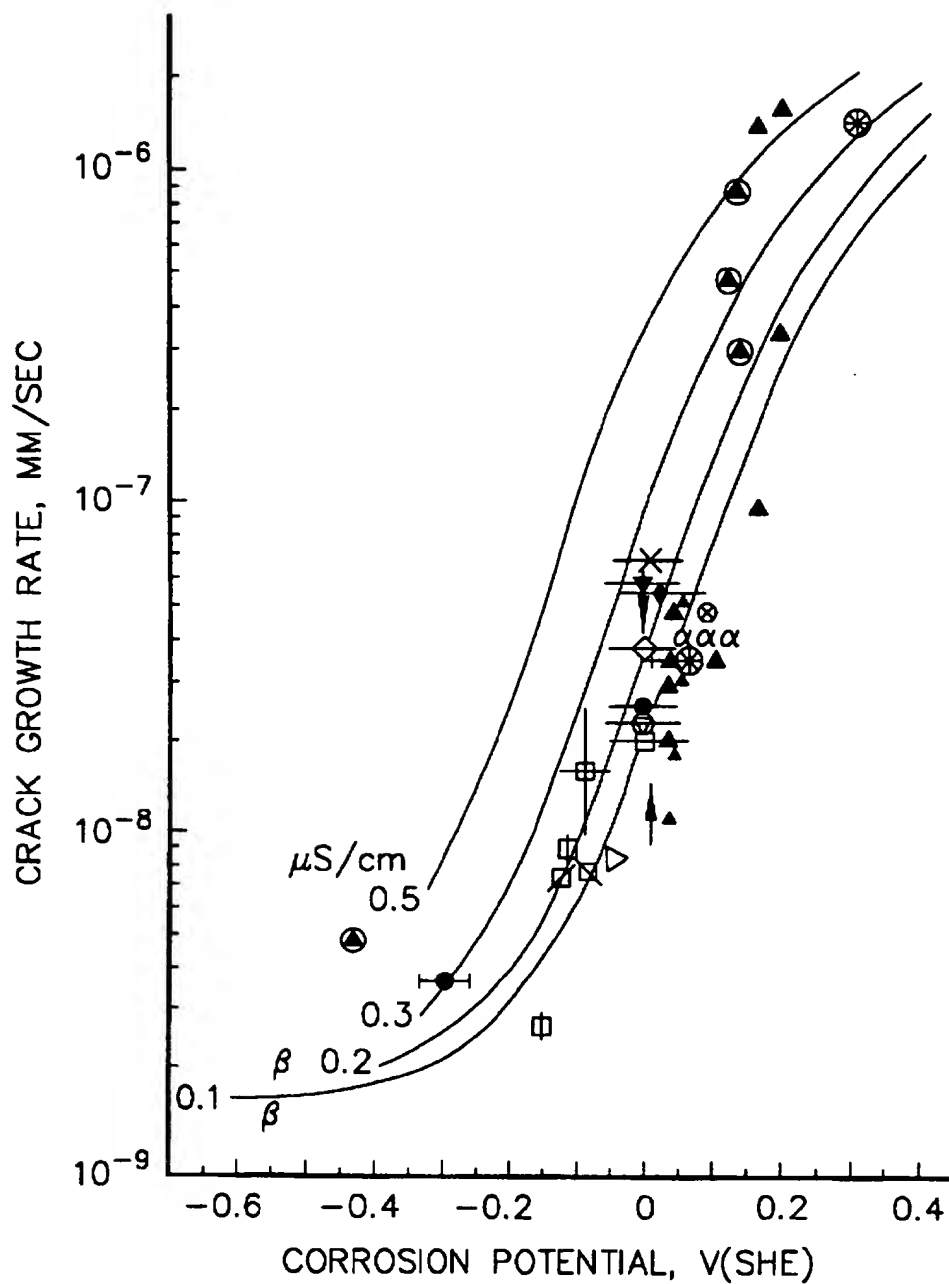


FIG. 1

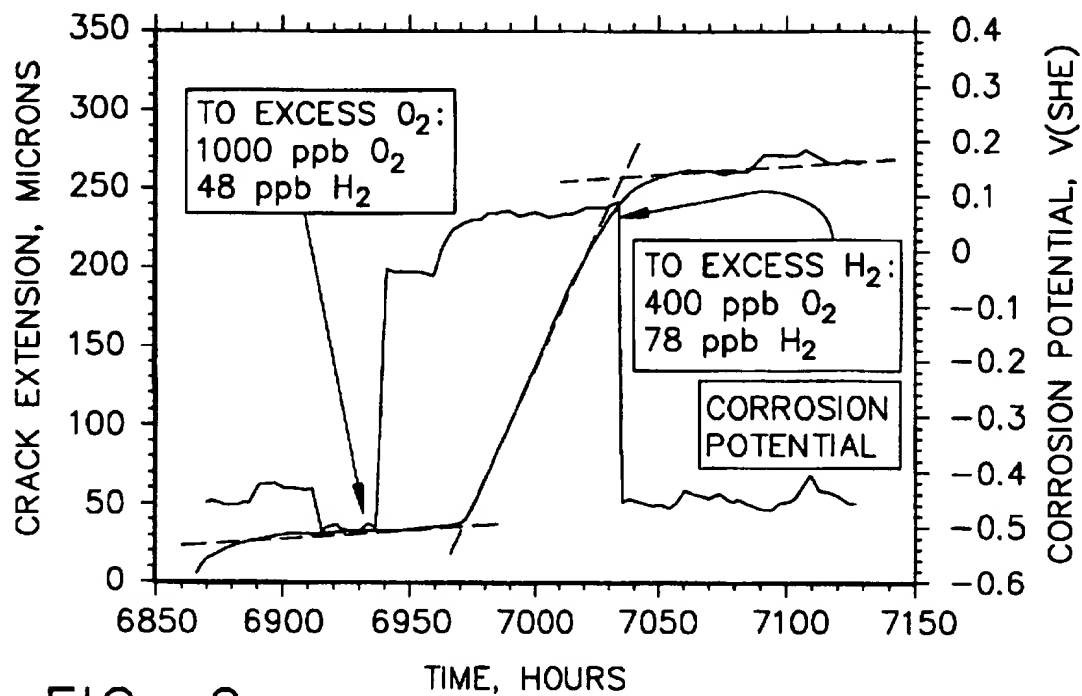


FIG. 2

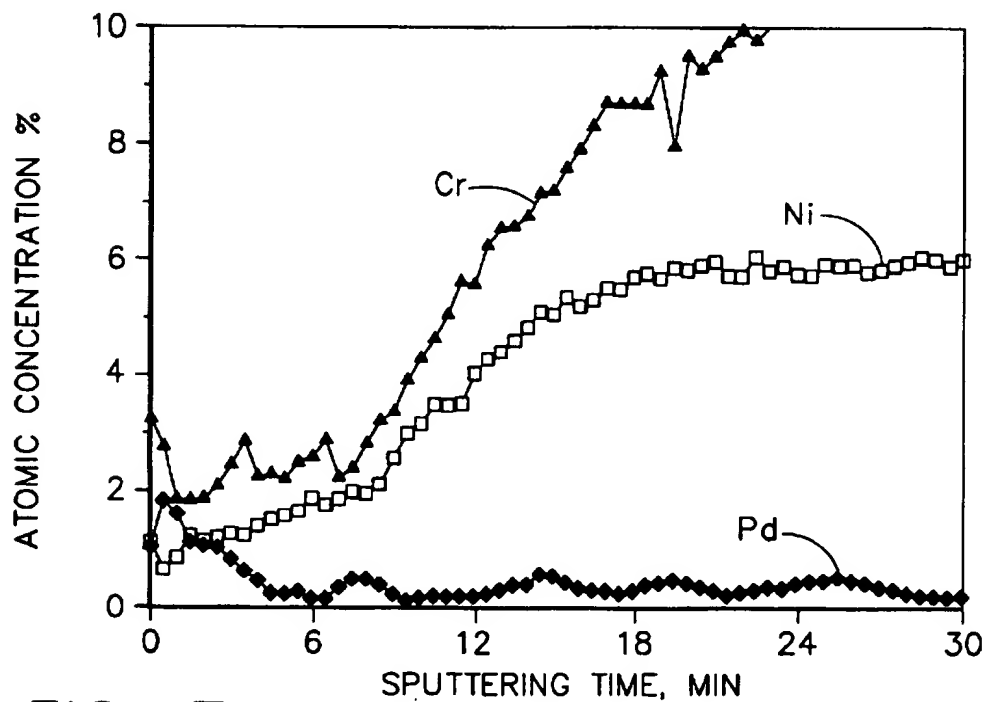


FIG. 7

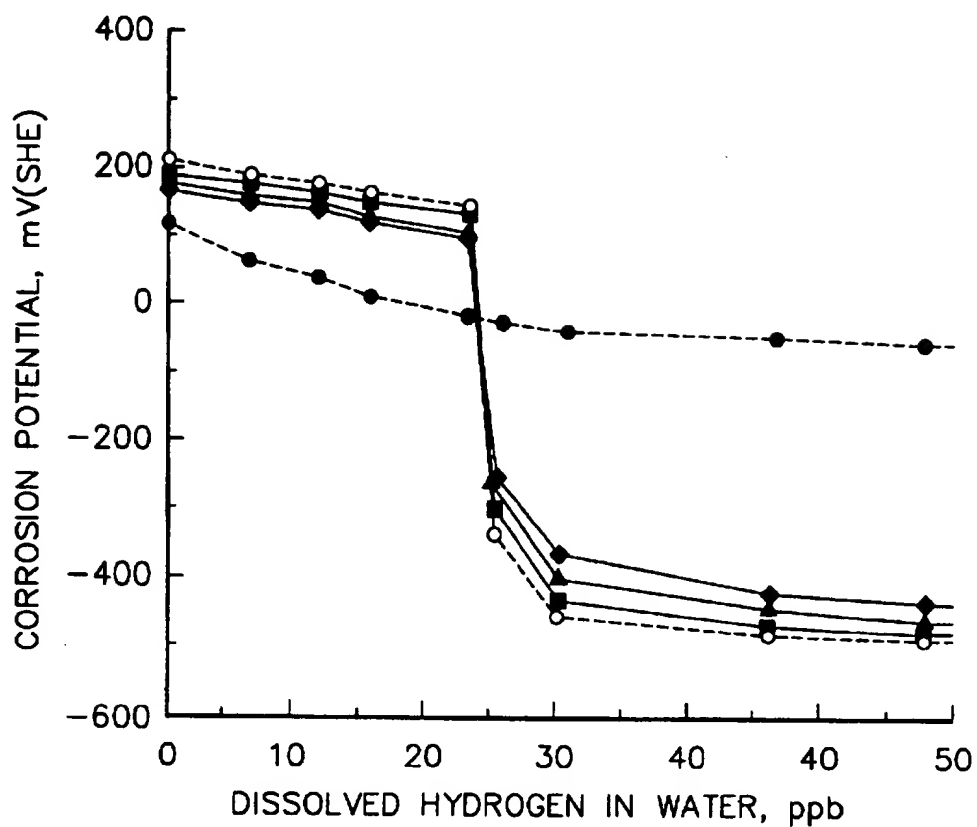


FIG. 3

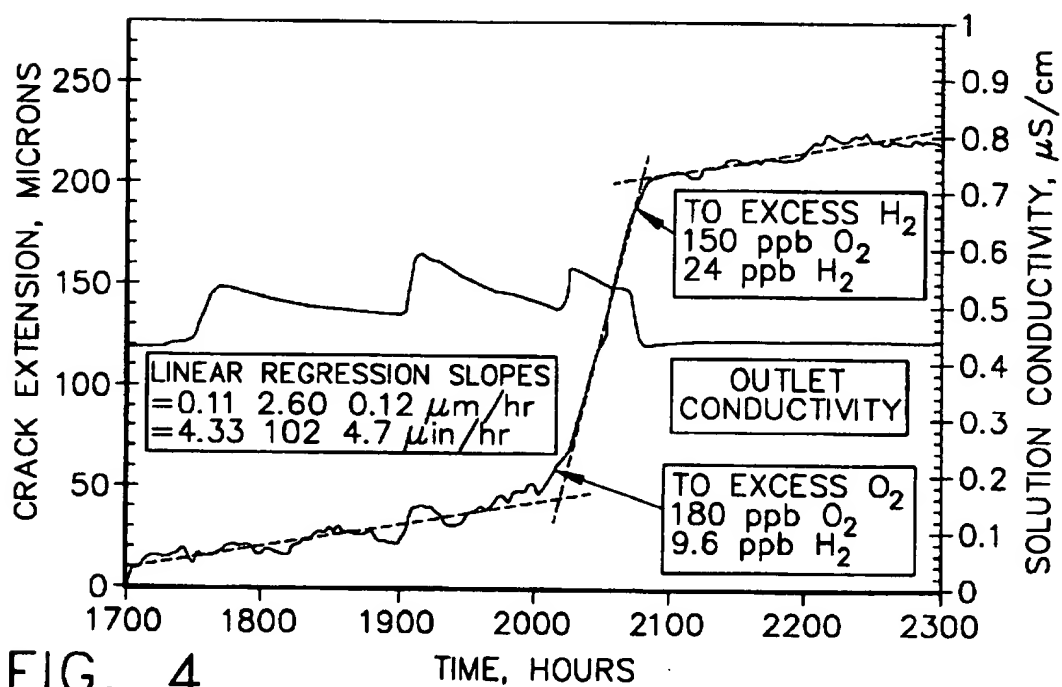


FIG. 4

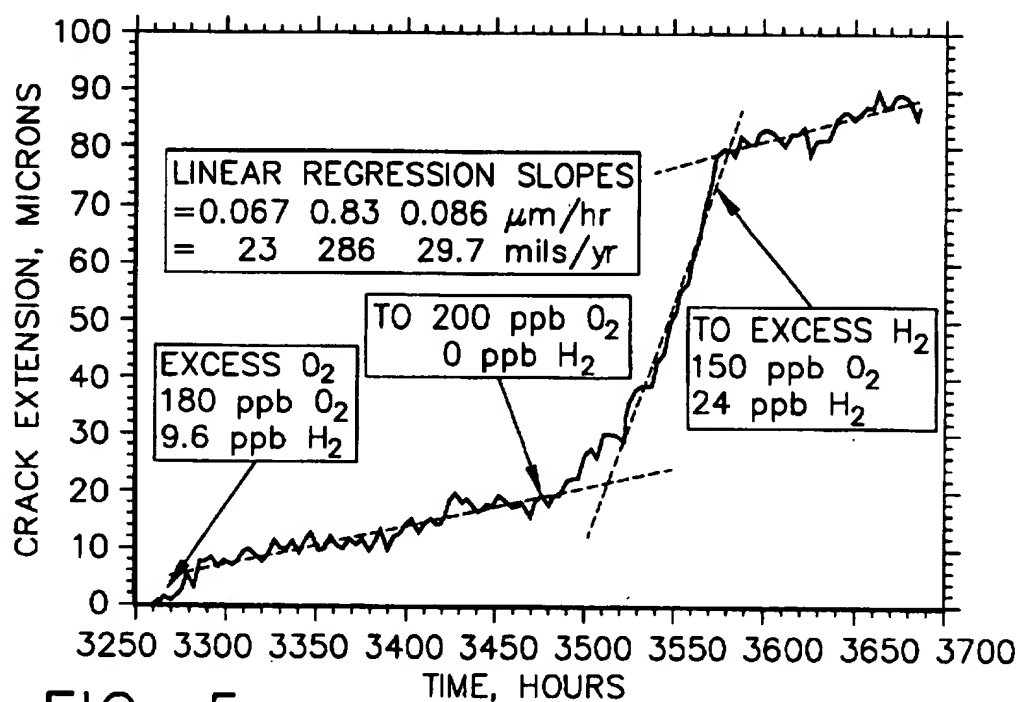


FIG. 5

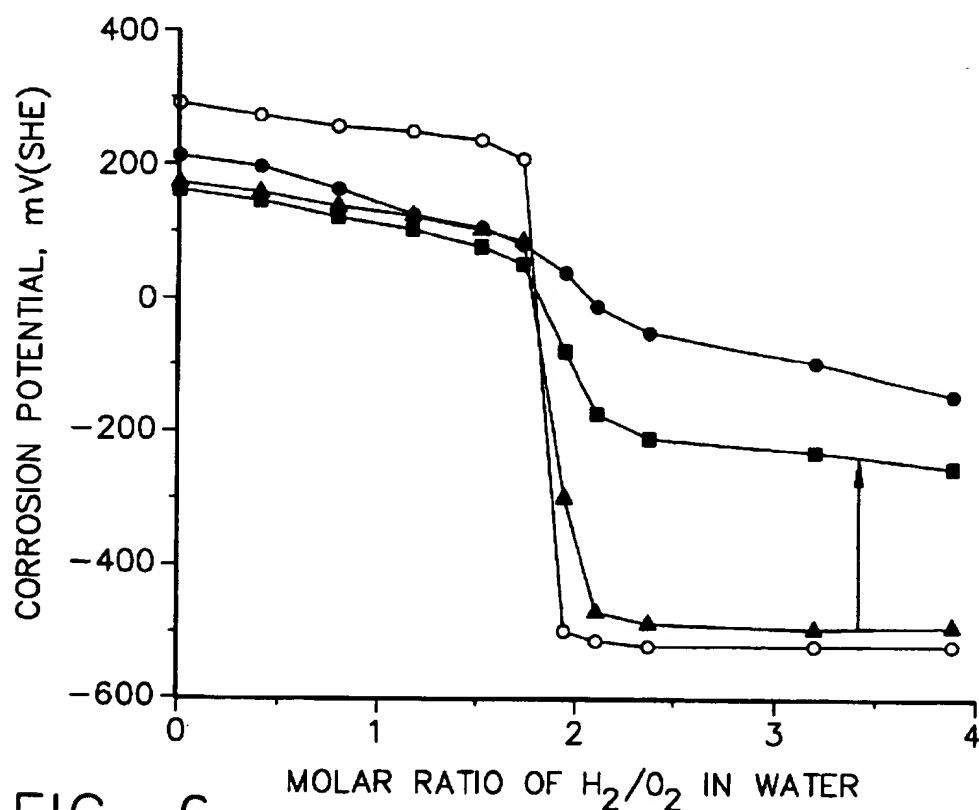


FIG. 6

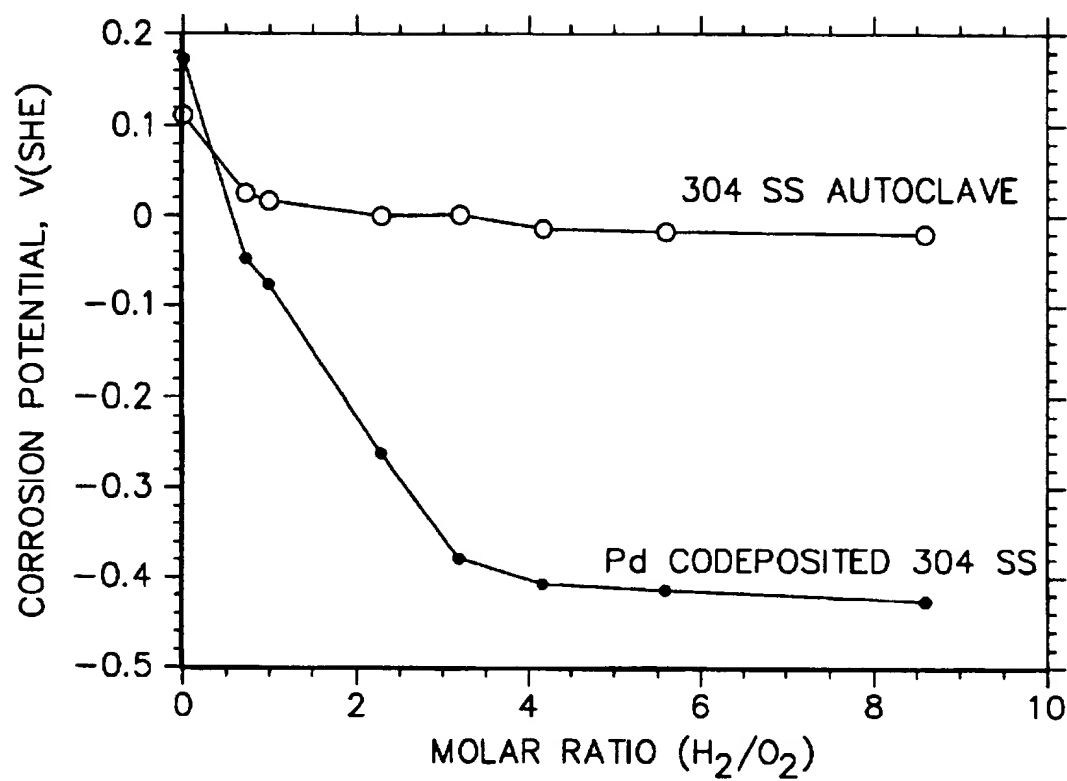


FIG. 8

CO-DEPOSITION OF PALLADIUM DURING OXIDE FILM GROWTH IN HIGH- TEMPERATURE WATER TO MITIGATE STRESS CORROSION CRACKING

RELATED PATENT APPLICATIONS

This application is a Rule 60 divisional of U.S. patent application Ser. No. 08/322,253, filed Oct. 13, 1994, now U.S. Pat. No. 5,608,766, which is a continuation-in-part of each of the following U.S. Pat. applications: Ser. No. 08/265,598, filed Jun. 24, 1994, now abandoned; Ser. No. 08/209,175, filed Mar. 10, 1994, now abandoned; Ser. No. 08/143,513, filed Oct. 29, 1993, now abandoned; and Ser. No. 08/143,514, filed Oct. 29, 1993, now U.S. Pat. No. 5,448,605.

FIELD OF THE INVENTION

This invention relates to reducing the corrosion potential of components exposed to high-temperature water. As used herein, the term "high-temperature water" means water having a temperature of about 150° C. or greater, steam, or the condensate thereof. High-temperature water can be found in a variety of known apparatus, such as water deaerators, nuclear reactors, and steam-driven power plants.

BACKGROUND OF THE INVENTION

A light-water nuclear reactor has a core of nuclear fuel which is cooled by recirculating water. A reactor pressure vessel contains the reactor coolant. Piping circuits carry the heated water or steam to the steam generators or turbines and carry circulated water or feedwater back to the vessel. Operating pressures and temperatures for the reactor pressure vessel are about 7 MPa and 288° C. for a boiling water reactor (BWR), and about 15 MPa and 320° C. for a pressurized water reactor (PWR). The materials used in both BWRs and PWRs must withstand various loading, environmental and radiation conditions.

Some of the materials exposed to high-temperature water include carbon steel, alloy steel, stainless steel, and nickel-based, cobalt-based and zirconium-based alloys. Despite careful selection and treatment of these materials for use in water reactors, corrosion occurs on the materials exposed to the high-temperature water. Such corrosion contributes to a variety of problems, e.g., stress corrosion cracking, crevice corrosion, erosion corrosion, sticking of pressure relief valves and buildup of the gamma radiation-emitting Co-60 isotope.

Stress corrosion cracking (SCC) is a known phenomenon occurring in reactor components, such as structural members, piping, fasteners, and welds, exposed to high-temperature water. As used herein, SCC refers to cracking propagated by static or dynamic tensile stressing in combination with corrosion at the crack tip. The reactor components are subject to a variety of stresses associated with, e.g., differences in thermal expansion, the operating pressure needed for the containment of the reactor cooling water, and other sources such as residual stress from welding, cold working and other asymmetric metal treatments. In addition, water chemistry, welding, heat treatment, and radiation can increase the susceptibility of metal in a component to SCC.

It is well known that SCC occurs at higher rates when oxygen is present in the reactor water in concentrations of about 5 ppb or greater. SCC is further increased in a high radiation flux where oxidizing species, such as oxygen, hydrogen peroxide, and short-lived radicals, are produced

from radiolytic decomposition of the reactor water. Such oxidizing species increase the electrochemical corrosion potential (ECP) of metals. Electrochemical corrosion is caused by a flow of electrons from anodic to cathodic areas on metallic surfaces. The ECP is a measure of the thermodynamic tendency for corrosion phenomena to occur, and is a fundamental parameter in determining rates of, e.g., SCC, corrosion fatigue, corrosion film thickening, and general corrosion.

In a BWR, the radiolysis of the primary water coolant in the reactor core causes the net decomposition of a small fraction of the water to the chemical products H_2 , H_2O_2 , O_2 and oxidizing and reducing radicals. For steady-state operating conditions, equilibrium concentrations of O_2 , H_2O_2 , and H_2 are established in both the water which is recirculated and the steam going to the turbine. These concentrations of O_2 , H_2O_2 and H_2 can result in conditions that promote intergranular stress corrosion cracking (IGSCC) of susceptible materials of construction.

As used herein, the term "critical potential" means a corrosion potential at or below a range of values of about -230 to -300 mV based on the standard hydrogen electrode (SHE) scale. IGSCC proceeds at an accelerated rate in systems in which the ECP is above the critical potential, and at a substantially lower or zero rate in systems in which the ECP is below the critical potential. Water containing oxidizing species such as oxygen and hydrogen peroxide increase the ECP of metals exposed to the water above the critical potential, whereas water with little or no oxidizing species present results in an ECP below the critical potential.

Thus, susceptibility to SCC in BWRs is highly influenced by corrosion potential. FIG. 1 shows the observed and predicted crack growth rate as a function of corrosion potential for furnace-sensitized Type 304 stainless steel at 27.5 to 30 MPa \sqrt{m} in 288° C. water over the range of solution conductivities from 0.1 to 0.5 $\mu S/cm$. Data points at elevated corrosion potentials and growth rates correspond to irradiated water chemistry conditions in test or commercial reactors. Reduction of the corrosion potential is the most widely pursued approach for mitigating SCC in existing plants.

One method employed to mitigate IGSCC of susceptible material is the application of hydrogen water chemistry (HWC) whereby the oxidizing nature of the BWR environment is modified to a more reducing condition. This effect is achieved by adding hydrogen gas to the reactor feedwater. When the hydrogen reaches the reactor vessel, it reacts with the radiolytically formed oxidizing species on metal surfaces to reform water, thereby lowering the concentration of dissolved oxidizing species in the water in the vicinity of metal surfaces. The rate of these recombination reactions is dependent on local radiation fields, water flow rates and other variables.

The injected hydrogen reduces the level of oxidizing species in the water, such as dissolved oxygen, and as a result lowers the ECP of metals in the water. However, factors such as variations in water flow rates and the time or intensity of exposure to neutron or gamma radiation result in the production of oxidizing species at different levels in different reactors. Thus, varying amounts of hydrogen have been required to reduce the level of oxidizing species sufficiently to maintain the ECP below the critical potential required for protection from IGSCC in high-temperature water.

It has been shown that IGSCC of Type 304 stainless steel used in BWRs can be mitigated by reducing the ECP of the

stainless steel to values below -0.230 V(SHE). However, high hydrogen additions, e.g., of about 200 ppb or greater, that may be required to reduce the ECP below the critical potential, can result in a higher radiation level in the steam-driven turbine section from incorporation of the short-lived N-16 species in the steam.

Thus, recent investigations have focused on using minimum levels of hydrogen to achieve the benefits of HWC with minimum increase in the main steam radiation dose rates.

An effective approach to achieve this goal is to either coat or alloy the stainless steel surface with palladium or any other platinum group metal. As used herein, the term "platinum group metal" means metals from the group consisting of platinum, palladium, osmium, ruthenium, iridium, rhodium, and mixtures thereof. The presence of palladium on the stainless steel surface reduces the hydrogen demand to reach the required IGSCC critical potential of -0.230 V(SHE). Compared to the HWC technique, which employs large hydrogen additions to suppress and recombine oxygen and hydrogen peroxide formed by radiolysis to very low levels (e.g., <2 ppb), the noble metal approach requires only that sufficient hydrogen be present so that, as water is formed on the catalytic surface, all oxygen and hydrogen peroxide are consumed (e.g., $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$). Additionally, lower potentials (generally the thermodynamic minimum) are obtained. Depending on the precise location within a BWR, the hydrogen addition required in the noble metal approach is reduced by a factor of 5 to 100.

The fundamental importance of corrosion potential versus, e.g., the dissolved oxygen concentration per se is shown in FIG. 2, where the crack growth rate of a crack growth specimen coated with palladium by electroless plating drops dramatically once excess hydrogen conditions are achieved, despite the presence of a relatively high oxygen concentration. FIG. 2 shows plots of crack length and corrosion potential vs. time for a Pd-coated crack growth specimen of sensitized Type 304 stainless steel showing accelerated crack growth in 288°C . water containing excess oxygen (e.g., 1000 ppb O_2 and 48 ppb H_2). Because the crack growth specimen was Pd-coated, the change to excess hydrogen (e.g., 400 ppb O_2 and 78 ppb H_2) caused the corrosion potential and crack growth rate to drop.

U.S. Pat. No. 5,135,709 to Andresen et al. discloses a method for lowering the ECP on components formed from carbon steel, alloy steel, stainless steel, nickel-based alloys or cobalt-based alloys which are exposed to high-temperature water by forming the component to have a catalytic layer of a platinum group metal. This layer catalyzes the recombination of reducing species, such as hydrogen, with oxidizing species, such as oxygen or hydrogen peroxide, that are present in the water of a BWR. Such catalytic action at the surface of the alloy can lower the ECP of the alloy below the critical potential where IGSCC is minimized. As a result, the efficacy of hydrogen additions to high-temperature water in lowering the ECP of components made from the alloy and exposed to the injected water is increased manifold. Furthermore, it is possible to provide catalytic activity at metal alloy surfaces if the metal substrate of such surfaces contains a catalytic layer of a platinum group metal. A solute can be provided by methods known in the art, for example by addition to a melt of the alloy or by surface alloying. Alternatively, a coating of platinum group metal provides a catalytic layer and catalytic activity at the surface of the metal. Suitable coatings can be deposited by methods well known in the art, such as plasma spraying, flame spraying, chemical vapor deposition, physi-

cal vapor deposition processes such as sputtering, welding such as metal inert gas welding, electroless plating, and electrolytic plating. However, these approaches are ex-situ techniques in that they cannot be practiced while the reactor is in operation.

The development of techniques to apply palladium in situ to all wetted components represents a breakthrough in extending the applications of the noble metal technology, since manual application (e.g., by thermal spray or fusion cladding) requires complex tooling, is slow and expensive, and can only coat surfaces to which there is sufficiently good access. U.S. patent applications Ser. Nos. 08/143,513, now abandoned, and 08/209,175, now abandoned, disclose a technique to coat or dope oxidized stainless steel surfaces in situ by injecting a metal-containing compound into the high-temperature water, which metal has the property of improving the corrosion resistance of those surfaces. The compound is injected in situ in the form of a solution or a suspension. The preferred compound for this purpose is palladium acetylacetonate, an organometallic compound. The concentration of palladium in the reactor water is preferably in the range of 5 to 100 ppb. Upon injection, the palladium acetylacetonate decomposes and deposits palladium on the oxidized surface. Palladium may be deposited within or on the surface of the oxide film in the form of a finely divided metal. The oxide film is believed to include mixed nickel, iron and chromium oxides.

The ECPs of the stainless steel components should all drop by ~ 300 mV after palladium injection. It is possible to reduce the ECP of Type 304 stainless steel to IGSCC protection values without injecting hydrogen provided that organics are present in the water. This occurs because of the catalytic oxidation of organics on Pd-doped surfaces.

Following palladium injection, hydrogen can be injected into the reactor water. As hydrogen is added, the potential of the Pd-doped oxide film on the stainless steel components is reduced to values which are much more negative than when hydrogen is injected into a BWR having stainless steel components which are not doped with palladium.

Other palladium compounds of organic, organometallic or inorganic nature, as well as compounds of other platinum group metals or non-platinum group metals such as titanium and zirconium, can also be used.

In summary, the oxygen content of the reactor water can be reduced by palladium injection alone initially. Some oxygen will be reduced by the organics of the organometallic palladium compound following thermal decomposition or radiolytic decomposition (induced by gamma and neutron radiation) of the organometallic palladium compound. When palladium injection is combined with hydrogen injection, oxygen will also be reduced as a result of the recombination of dissolved oxygen and hydrogen molecules at the Pd-doped surfaces forming water molecules.

The effectiveness of alloys or coatings that contain at least about 0.1% noble metal (which category of metals is also referred to in the art as "platinum group metals") has been extensively demonstrated. The data presented in FIG. 3 were obtained using pre-oxidized Type 304 stainless steel electrodes held in 288°C . water containing 300 ppb O_2 for 8 months. The presence of platinum reduced the corrosion potential of Type 304 stainless steel for dissolved hydrogen levels in excess of about 24 ppb. The amount of platinum was varied as follows: (•) no Pt; (◊) 0.1% Pt; (▲) 0.35% Pt; (■) 1.0% Pt; (○) pure Pt.

In situ palladium deposition from aqueous solutions on pre-oxidized materials has also been shown to be effective.

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both in terms of deposition (the presence of palladium on the surface has been confirmed by Auger electron spectroscopy and X-ray photoelectron spectroscopy) and catalytic response (in high-temperature water containing stoichiometric excess hydrogen). FIG. 4 shows a plot of crack length and solution conductivity vs. time for a Pd-coated crack growth specimen of furnace-sensitized Type 304 stainless steel showing accelerated crack growth in 288° C. water containing about 180 ppb O₂ and 9.6 ppb H₂. Because the crack growth specimen was Pd-coated (i.e., in shallow water by the high-velocity oxy-fuel technique with Type 309L stainless steel +0.42% Pd), the change to excess hydrogen (i.e., 150 ppb O₂ and 24 ppb H₂) caused the corrosion potential and crack growth rate to drop.

FIG. 5 is a plot of crack length vs. time for a Pd-doped crack growth specimen of furnace-sensitized Alloy 182 weld metal showing accelerated crack growth in 288° C. water containing excess oxygen and reduced crack growth under excess hydrogen conditions in the presence of palladium. Palladium doping was performed on a pre-oxidized (and previously tested) crack growth specimen from a 100 ppb (as Pd) aqueous solution of palladium acetylacetonate. The specimen was first exposed to zinc and then Pd-doped for 48 hr.

However, it has also been shown that exposure to prolonged ultrasonic cleaning significantly reduces both the presence of palladium and the surface catalytic response. FIG. 6 shows a significant reduction in the catalytic effectiveness of in-situ palladium deposition in reducing the corrosion potential in 288° C. water under stoichiometric excess hydrogen conditions following prolonged exposure to ultrasonic cleaning. Deposition was performed on a pre-oxidized coupon specimen from a 100 ppb (as Pd) aqueous solution of palladium acetylacetonate. FIG. 6 shows corrosion potential as a function of H₂/O₂ molar ratio for the following materials in 288° C. water having 1.0 ppm O₂: (•) undoped Type 304 stainless steel; (▲) Pd-doped Type 304 stainless steels doped by in situ deposition and not exposed to ultrasonic cleaning; (■) Pd-doped Type 304 stainless steels doped by in situ deposition and then exposed to 60° C. water for 1 week in an ultrasonic bath; and (○) pure platinum. The Pd-doped specimen showed a 250 mV increase in ECP after being exposed to ultrasonic cleaning. These results indicate the loss of the surface catalytic property.

SUMMARY OF THE INVENTION

The present invention is a method for improving the performance and longevity of coatings of noble metal or any other metal deposited from aqueous solutions of inorganic, organic or organometallic compounds. In particular, the invention is a method of distributing a desired metal throughout the thickness of an oxide film formed on nuclear reactor components. The method of the invention optionally includes the step of removing some or all of the oxide film on the surface of a reactor component in situ and then co-depositing metal, e.g., palladium, during subsequent growth of the oxide film. In cases where the deposited metal is a noble metal, e.g., palladium, the result of this technique is a noble metal-doped oxide film having a relatively longer catalytic life in the reactor operating environment.

The concept of the present invention involves preparation by environmental, mechanical or decontamination exposure of a pre-oxidized metal surface and/or exposure to aqueous metal compounds during subsequent oxide film growth to incorporate the metal, e.g., palladium or zirconium, into the

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oxide film. Incorporation of palladium or zirconium into the film provides greatly increased longevity of the corrosion inhibition effect as compared to palladium or zirconium coatings which lie on the oxide surface or penetrate only a thin stratum at the oxide surface.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the observed and predicted crack growth rate as a function of corrosion potential for furnace-sensitized Type 304 stainless steel in 288° C. water over the range of solution conductivities of 0.1–0.5 μS/cm.

FIG. 2 shows plots of crack length and corrosion potential vs. time for a Pd-coated crack growth specimen of sensitized Type 304 stainless steel in 288° C. water for excess oxygen and excess hydrogen conditions.

FIG. 3 is a plot showing the ECPs of platinum, Pt-doped Type 304 stainless steel containing various levels of platinum and undoped Type 304 stainless steels in 288° C. water containing 300 ppb O₂ as a function of the amount of dissolved hydrogen.

FIG. 4 shows plots of crack length and solution conductivity vs. time for a Pd-coated crack growth specimen of sensitized Type 304 stainless steel in 288° C. water for excess oxygen and excess hydrogen conditions. The Type 304 stainless steel was thermally sprayed by the hyper velocity oxy-fuel (HVOF) technique with a powder of Type 309L stainless steel containing 0.42% Pd.

FIG. 5 is a plot of crack length vs. time for a Pd-doped crack growth specimen of furnace-sensitized Alloy 182 weld metal showing accelerated crack growth in 288° C. water containing excess oxygen and reduced crack growth under excess hydrogen conditions in the presence of palladium deposited in situ.

FIG. 6 is a plot showing the ECPs of undoped Type 304 stainless steel (•), Pd-doped Type 304 stainless steels doped by in situ deposition and not exposed to ultrasonic cleaning (▲), Pd-doped Type 304 stainless steels doped by in situ deposition and then exposed to ultrasonic cleaning (■), and pure platinum (○) in 288° C. water as a function of the H₂/O₂ molar ratio.

FIG. 7 is an Auger electron spectroscopy depth profile for Cr (▲), Ni (□) and Pd (•) of the as-exposed surface of as-machined Type 304 stainless steel exposed in 288° C. water containing about 300 ppb O₂ and 100 ppb Pd as palladium acetylacetonate, palladium doped by the co-deposition technique.

FIG. 8 is a plot showing the ECPs of a palladium co-deposited specimen of Type 304 stainless steel (•) and a Type 304 stainless steel autoclave (○) as a function of the H₂/O₂ molar ratio.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiment of the present invention is a technique to dope stainless steel surfaces with palladium in situ by injecting a palladium-containing compound into the high-temperature water of a BWR while oxide film is forming on the stainless steel surface. Preferably the palladium compound is injected in the form of a solution or suspension at a point upstream of the feedwater inlet. The high temperatures as well as the gamma and neutron radiation in the reactor core act to decompose the compound, thereby freeing palladium species for incorporation in the oxide film as it grows. As used herein, the term "species" means ions or atoms. One Pd-containing compound suc-

cessfully used for this purpose is an organometallic compound, palladium acetylacetonate. However, other noble metal compounds of organic, organometallic and inorganic nature can also be used for this purpose. The palladium acetylacetonate compound is dissolved in an ethanol/water mixture or in water alone to form a solution or suspension which is injected into the reactor coolant.

The palladium gets incorporated into the stainless steel oxide film via a thermal decomposition process of the organometallic compound. As a result of that decomposition, Pd species become available to replace atoms, e.g., Fe atoms, in the oxide film, thereby producing a Pd-doped oxide film on stainless steel.

The method of the present invention involves in situ removal of some or all of the oxide film from the surfaces of wetted reactor component and co-deposition of noble metal during subsequent growth of oxide film on the same wetted surfaces. The result is a noble metal-doped oxide film having a relatively longer catalytic life in the reactor operating environment. Incorporation of palladium into the film provides greatly increased catalytic life as compared to palladium coatings which lie on the oxide surface.

In accordance with the broad concept of the present invention, several approaches are possible. In the simplest approach, mechanical cleaning (e.g., by flapper wheel or ultra-high-pressure water jet) is used to remove most or all of the oxide film from the reactor component to be treated. Because the oxide film formed on a reactor component reaches a limiting thickness, some portion of the oxide film must be removed before more oxide film, which forms the matrix for the metal dopant, can be grown. After removal of some oxide film, the appropriate aqueous noble metal compound is added to the reactor water prior to initial heat up. This can be accomplished without the nuclear fuel being present by using the recirculation pumps. As the oxide film reforms, palladium will be incorporated into the film. While it is desirable to use the highest possible palladium concentrations consistent with plant and cost considerations, levels in the preferred range of 5 to 100 ppb Pd should be sufficient.

In accordance with the preferred method, after the oxide film has been thinned, noble metal doping of newly formed oxide film can be performed at regular intervals to produce a noble metal concentration which varies cyclically in the thickness direction or can be performed continuously to produce a noble metal concentration which is generally constant in the thickness direction.

Since mechanical cleaning is expensive, complex and limited to reactor components that are readily accessible, more attractive approaches for preparing the oxidized alloy surfaces include chemical decontamination (which is periodically performed in many plants to reduce the radioactivity, e.g., of piping from Co⁶⁰ and other elements which incorporate into the oxide) and exposure to hydrogen water chemistry, which will thin the existing oxide film. Additions of zinc will also reduce the oxide film thickness. However, it may be desirable to halt the zinc additions during the palladium doping process since zinc appears to densify the film. The formation of ZnO on alloy surfaces has been shown to yield many benefits in BWRs, including reduced incorporation of Co60 in films (thereby lowering the radiation level, e.g., in piping) and reduced susceptibility to SCC.

A further aspect of the present invention is that cycling the temperature during the palladium doping process (e.g., by repeatedly raising the water temperature to 550° F. and then cooling the water to 100° F.) should be beneficial, since the

solubility of the metal oxides, film thickness and semiconducting properties of the oxide film change with change in temperature. This may be especially valuable following zinc exposure, since zinc desorbs from the oxide films at lower temperatures, providing more sites for the deposition of palladium and more opportunities for film growth.

The advantage of the method of the invention, in which the oxide film on alloy surfaces is removed or thinned before palladium deposition, is that palladium is distributed throughout the oxide film in the thickness direction. In contrast, when pre-oxidized alloy surfaces are treated with, e.g., palladium acetylacetonate, the palladium is deposited only on the surface of the oxide. If this deposited palladium is removed from the surface, e.g., by very high flow rates of the reactor coolant, the catalytic response of the surface coating with palladium is decreased, whereas in the case of co-deposition of palladium during oxide film growth, the catalytic response may be sustained due to the presence of palladium species throughout the thickness of the oxide film.

Cylindrical coupons of as-machined Type 304 stainless steel were exposed in 288° C. water containing about 300 ppb O₂ for 16 hr. Thereafter, the coupons were exposed in 288° C. water containing about 300 ppb O₂ and 100 ppb Pd as palladium acetylacetonate for 6-8 hours. This cycle was repeated six times. During palladium doping cycles, palladium acetylacetonate was injected. During oxidizing cycles, palladium acetylacetonate was not injected and the palladium acetylacetonate injected during the doping cycle had been removed by the water cleanup system. During the doping cycle, palladium deposits on the high-temperature oxide film and as this oxide film thickens over time, palladium is incorporated throughout the layer of oxide in the thickness direction. However, the palladium concentration in the thickness direction of the oxide film varies as a function of the amount of palladium in the solution in which the coupon is exposed.

During this experiment, the incorporation of palladium was observed by depth profiling the Auger electron spectroscopy of the as-exposed surface. The cyclical variation of the palladium doping in the thickness direction can be seen in FIG. 7. The excellent corrosion potential response of this palladium co-deposited specimen is shown in FIG. 8 by the sharp decrease in corrosion potential at H₂/O₂ molar ratios in the range of about 1.5-2.

The method of the present invention can also be used to dope oxide films on reactor components with corrosion-inhibiting non-noble metal. In accordance with this method, the component or structural material is immersed in a solution or suspension of a compound containing the non-noble metal. The non-noble metal must have the property of increasing the corrosion resistance of the stainless steel or other metal surface when incorporated therein or deposited thereon. The selected compound must have the property that it decomposes under reactor thermal conditions to release species of the selected non-noble metal which incorporate in or deposit on the oxide film formed on the stainless steel or other metal surfaces. The non-noble metals which can be used are selected from the group consisting of zirconium, niobium, yttrium, tungsten, vanadium, titanium, molybdenum, chromium and nickel. The preferred compounds in accordance with the invention are those containing zirconium, e.g., the organometallic compounds zirconium acetylacetonate and inorganic compounds zirconium nitrate and zirconyl nitrate.

The present invention offers the advantage that alloy surfaces can be doped with palladium or other metal using

an in-situ technique (while the reactor is operating) which is simple in application and also inexpensive. However, this technique can also be implemented for coating ex-situ components. In addition, the technique can be applied to operating BWRs and PWRs and their associated components, such as steam generators.

The foregoing method have been disclosed for the purpose of illustration. Variations and modifications of the disclosed method will be readily apparent to practitioners skilled in the art of mitigating stress corrosion cracking. For example, noble metals other than palladium can be applied using this technique. The noble metal can be injected in the form of an organic or inorganic compound in conjunction with injection of small amounts of hydrogen to reduce the potential of stainless steel reactor components. One option is to inject the palladium acetylacetonate solution or suspension via the same port by which dissolved hydrogen is injected. The corrosion-inhibiting non-noble metals can be used even in the absence of hydrogen injection. In addition, the doping technique of the invention is not restricted to use with stainless steel surfaces, but also has application in reducing the ECP of other metals which are susceptible to

IGSCC, e.g., nickel-based alloys. All such variations and modifications are intended to be encompassed by the claims set forth hereinafter.

We claim:

1. A nuclear reactor component made of an alloy and having an oxide film formed on its surface, wherein said oxide film has incorporated therein a species of a metal having the property of increasing the corrosion resistance of said alloy when incorporated in said oxide film, said metal species being a noble metal or a non-noble metal selected from the group consisting of zirconium, niobium, yttrium, tungsten, vanadium, titanium and molybdenum, said metal species having a concentration throughout the oxide film sufficient to reduce the corrosion potential at the surface of said oxide film to below a critical potential conducive to stress corrosion cracking even as the surface of said oxide film is gradually removed and a new surface is exposed.

2. An alloy component as defined in claim 1 wherein said metal species is a noble metal.

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